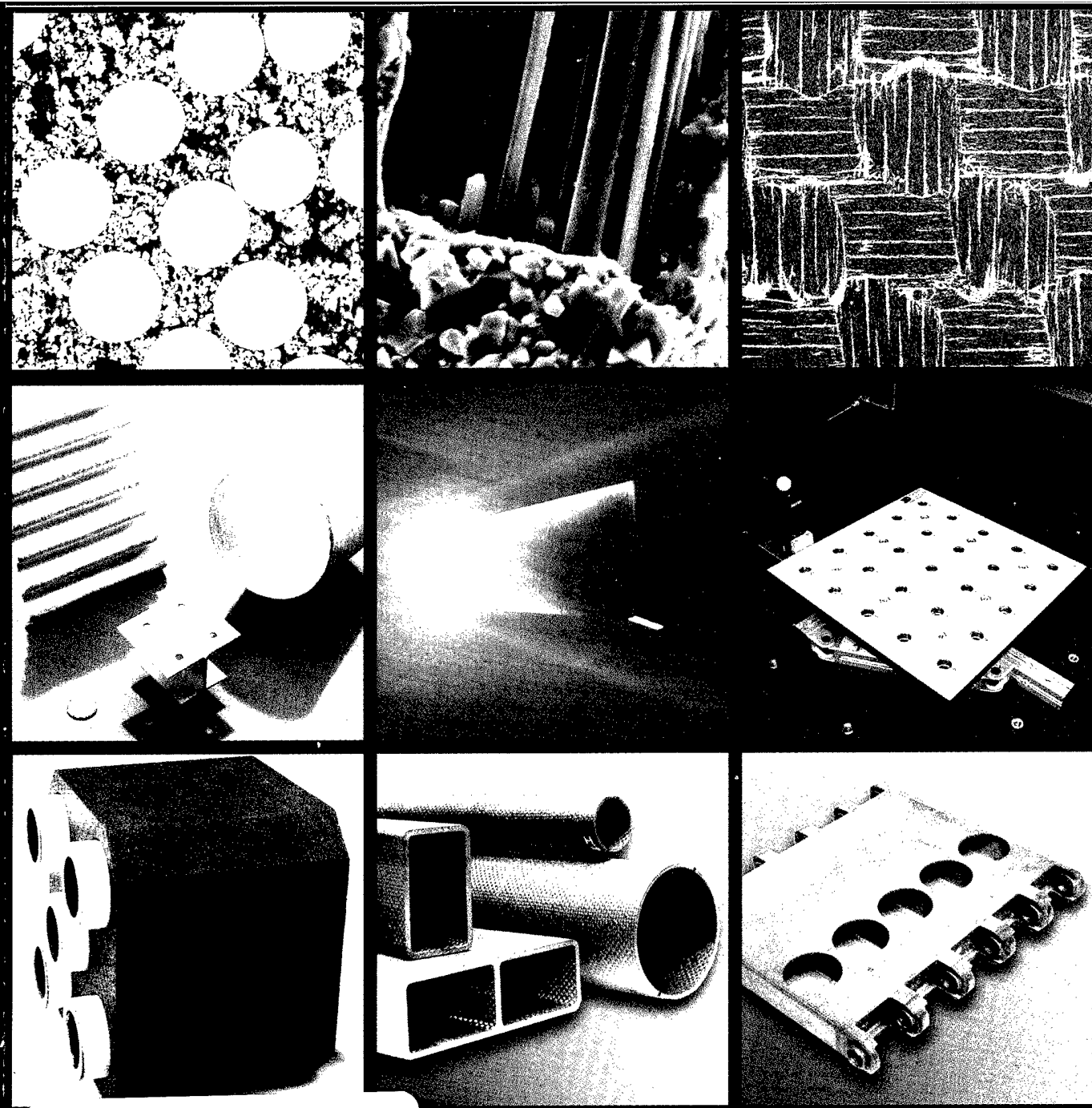


1-3 October 2001, Munich, Germany

HT-CMC 4



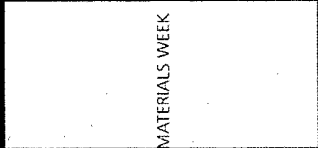
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# Book of Abstracts

4<sup>th</sup> International Conference on  
High-Temperature  
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## Preface

The HT-CMC Conference series was created in 1993 to promote the exchange of information, data and research advances between academia and industry on ceramic matrix composites (CMCs) for applications in very severe environments (such as rocket engines or spacecraft heat shields). Generally speaking, these first applications required only short lifetime materials, typically from a few minutes to a few hours, such as those made of carbon (or eventually SiC) fibers embedded in a carbon or SiC matrix. At that time, the conference mainly focused on basic topics: processing, fiber-matrix interface, mechanical behaviour, in order to identify the key concepts and behaviours. Then, the scope of the conference was progressively broadened as more performant materials became available (oxygen-free SiC fibers, multilayered interphases, self-healing non-oxide matrices, oxide/oxide materials) and new applications requiring long lifetime materials were identified, such as hot parts for aeronautical engines or gas turbines for power generation.

The first meetings of the series were held in Bordeaux (1993), Santa Barbara (1995) and Osaka (1998). Two of them have been organized in conjunction with other conferences (ECCM-6 in Bordeaux; EnCera '98 in Osaka) on related subjects, in order to promote the exchange between the monolithic ceramics and composites communities. Additionally, the meetings have been organized in areas where there is a strong R&D activity in the field of CMCs.

HT-CMC-4 is organized on the same basis and in conjunction with the larger conference Materials Week, and the exhibition MATERIALICA. It is also characterized by several innovations with respect to the former conferences. Firstly, it focuses on applied research and applications since CMCs are now matured materials (although the basic aspects are also treated). Secondly, the classical short oral communication sessions are replaced by keynote lectures and poster forums with more time devoted to discussion between the authors and the conference attendees. Finally, HT-CMC 4 may well be, from the number of abstracts received, the largest conference of the series, which shows how dynamic this branch of Materials Science and Engineering has become in ten years. We wish you a pleasant and exciting experience, and we are looking forward to seeing you in Munich!

Munich, October 2001

W. Krenkel  
R. Naslain  
H. Schneider

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## HT-CMC 4 Time Schedule

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09:50 - 10:40	Poster introduction	09:30 - 10:40	Poster introduction	Poster introduction
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13:50 - 14:20	Keynote lecture	13:50 - 14:20	Keynote lecture	Keynote lecture
14:20 - 15:25	Poster introduction	14:20 - 15:25	Poster introduction	Poster introduction
15:25 - 16:40	Scientific forum <b>Fibres</b>	15:25 - 16:40	Scientific forum <b>Non-oxide CMCs: processing</b>	Scientific forum <b>Applications</b>
16:40 - 17:10	Keynote lecture	16:40 - 17:10	Keynote lecture	Keynote lecture
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**Sunday, 18:30 - 20:30:** Welcome reception by Lord Mayor of Munich

# Conference Organisation

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# **Oxide/oxide CMCs**

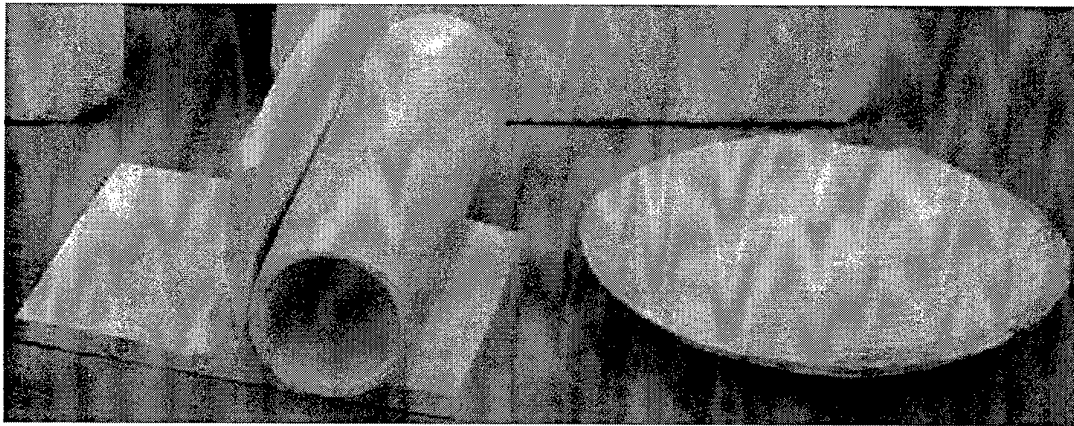
**Monday, October 1<sup>st</sup>**  
**Morning session**

## Oxide/Oxide Composites: Control of Microstructure and Properties

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Fibers are strong because the largest flaw perpendicular to the direction in which they are stressed can be no larger than the fiber diameter itself. Since the failure strain of a strong fiber is much larger than the surround matrix, crack extension initiates within the matrix. One requirement of a CMC is that the fibers must be isolated from the very high stress field of a matrix crack. A fiber within a good CMC is only expected to fail when the applied stress exceeds its strength.

Conventional CMCs, have crack deflecting interfaces (or interphases) that isolate the matrix cracks from the fibers. During the initial loading, the stress-strain behavior is linear and characterized by the combined elastic modulus of the fibers and matrix. As loading proceeds, matrix cracking initiates without fiber failure. Matrix cracking is manifested by the on-set of nonlinearity in the stress-strain response. A second approach has emerged; it involve the use of a porous matrix. Unlike CMCs with crack-deflecting interfaces and nominally dense matrices, the porous matrix CMCs allow matrix and fibers to be bonded together and still achieve the damage tolerance of conventional CMCs. Despite these changes, which are not taught by the mechanics of conventional CMCs, the strength of these "new" CMCs exhibit similar notch insensitivity as the conventional materials. In addition, their failure strain is larger than that of conventional monolithic ceramics, although in their present generation, not as high as the conventional CMCs. Also important is that the new CMCs are much easier to process because the matrix need not be made dense, and an interphase between the fiber and matrix is not needed to produce a crack deflecting interface. The failure mode of the porous matrix composites is different from the conventional CMCs. Matrix cracking occurs throughout the entire loading range, but the tensile stress/strain behavior of specimens is nearly linear to failure. Tensile failure of multi-laminates occurs with a relatively notch insensitive strength. Because the strength and toughness of the porous matrices are less relative to dense matrices, the interlaminar shear strength is less, relative to dense matrix composites of the same nature. The oxide-oxide composites are relatively stable in air up to temperatures at which the fibers begin to degrade. Processing of the new CMCs, detailed here, is much more rapid than the conventional CMC's, and they can be made as large engineering components, e.g., tubes, T sections, etc. shown below for a mullite/alumina fiber CMC, that are difficult to process as monoliths.



## Processing and Properties of Oxide/Oxide Composites for Industrial Applications

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**Keywords:** oxide fibers, oxide matrix, weak interface, manufacturing techniques, high temperature long-term stability, aeroengines, power plants, spacecraft heat shields

Conventional oxide ceramics are resistant to high temperatures, show high hardness, as well as compressive strength even under chemically severe conditions. They are used for a variety of industrial products, e. g. cutting tools, catalyst carriers, bearings of pumps, furnace components, medical implants or electronic constituents. Compared to metals, they mostly are of lower density but of higher brittleness. This brittleness, up to now, did not allow their use under extreme mechanical loads especially in the tensile mode. From non-oxide materials, it is well known that reinforcement with continuous fibers can drastically reduce the brittleness. In principle, the same reinforcement mechanisms can be applied to oxide ceramics. As a consequence, a lot of developers world-wide are working on this topic. Their common objective is to manufacture a material with high strength and damage tolerance, which can be applied at temperatures higher than 1200 °C and for several thousand hours. This group of materials is attractive for future components of power plants, aeroengines, chemical reactors and also for spacecraft heat shields. It allows higher operating temperatures compared with metals and thus enables better performance or improved fuel efficiency.

Oxide/oxide composites must have fibers, a matrix and an interface between fiber and matrix, all three of which are thermodynamically stable. The fibers with the best stability are of single crystal type, e.g. out of alumina or yttrium aluminium garnet but they are rather expensive and not available in an industrial scale. Polycrystalline fibers already commercially available (such as the Nextel™ types) are based on alumina or alumina/silica compositions. They can be used up to temperatures of 1100 °C, for higher values, however, their life-time is limited because of grain growth. As a matrix, alumina and mullite are suitable compositions. Because of higher creep resistance, most developers prefer alumina/silica compositions near to mullite stoichiometry. For allowing damage-tolerant behavior under mechanical loads by the fiber-pull-out effect, interface microstructures enabling weak bonding between fiber and matrix are used. This effect can be accomplished with pores respectively a gap at the interface or interlayers with cleavable oxide phases such as calcium or lanthanum hexaluminates. Meanwhile, best prototype materials having a 0°/90° fiber reinforcement achieve a tensile strength in the range of 200 MPa and an elongation to break of about 0.4 %.

Depending on the composition of the matrix and the chemistry of the raw materials, different manufacturing processes have been developed. Infiltration of the fibers is usually performed at room temperature by use of slurries or precursor liquids. Subsequently, the pre-ceramic composite body is heat treated in order to synthesize the matrix phase by sintering, pyrolysis, reaction bonding or similar processes. High temperature pressing generates rather dense bodies, but is limited to small and simple geometries because of cost reasons. Techniques which do not need high pressures and high temperatures at the same time, are more economic, especially if they allow net shape production. Examples for these procedures are polymer infiltration and pyrolysis (PIP) and powder slurry infiltration techniques combined with reaction sintering. Using these processes, first prototype components for aeroengines, spacecraft as well as for power plants were manufactured (by various developers) and showed some promising test results. More details about materials, processes and prototype components will be presented during the HT-CMC 4 Conference and will be described within the proceedings.

## Nextel 480/Silica Composites by Atmosphere Pressure Chemical Vapor Infiltration

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**Keywords:** Nextel 480, reinforced, silica matrix composites, Tetraethylorthosilicate, APCVI

Continuous oxide fiber reinforced oxide matrix composites are attractive for use as high temperature structural materials because they can combine composite properties with long-term stability in oxidizing atmosphere.  $\text{SiO}_2$  ceramic, which combines resistance to ablation with stability to dielectric in high temperature, is the ideal dielectric-thermal-protective materials used as warhead and antenna window of missile. At present, three-dimension oxide fiber preform reinforced  $\text{SiO}_2$  ceramic matrix composites were manufactured by impregnation in colloidal aqueous silica sol repeatedly. Laminates composites were fabricated using polymer infiltration pyrolysis (PIP) of the Blackglas resin and ceramic fabric lay-up. The two methods all are very complex.

In this paper, the fiber preform of Nextel 480, which is a mullite composition containing 70% alumina, 28% silica, and 2% boria, was used as reinforcement. Nextel 480/Silica Composite was manufactured by Atmosphere Pressure Chemical Vapor Infiltration (APCVI). CVI is a near net shape and flexible process, which can be applied to preforms of complex and different shapes. Tetraethylorthosilicate (TEOS) was used as precursor. Ar was used as carrier gas. The effect of deposition temperature on deposition rate and deposition effect was investigated in detailed. The microstructure of the Nextel 480/Silica composite was analyzed.

XRD results exhibit that the deposition production, deposited below  $800^\circ\text{C}$ , is amorphous silica. Experiment result shows the deposition rate of  $\text{SiO}_2$  increases with increasing temperature around  $400\sim 750^\circ\text{C}$  and decreasing the inside diameter of the deposition furnace, which proves that the deposition procedure is decided by mass transfer controlling from  $400\sim 750^\circ\text{C}$ . Mass transfer controlling is benefit to get conform deposition production. The microstructure of the cross section surfaces of the composites at  $750^\circ\text{C}$  for 60h shows the filament fibers were surrounded uniformly by  $\text{SiO}_2$  matrix and no pore was found in the  $\text{SiO}_2$  matrix, which indicates the matrix is very dense. There are no cracks on the surface of the  $\text{SiO}_2$  matrix. This indicates the thermal expansion coefficient of the  $\text{SiO}_2$  matrix deposited at  $750^\circ\text{C}$  matches with the Nextel 480 fiber.

Microstructure SEM photographs show deposition effect was affected by deposition temperature dramatically. The single filament is distinct on the surface of the specimen deposited at  $750^\circ\text{C}$  for 60h, but slur at  $800^\circ\text{C}$ . Much white coarse powders were founded on the surface of the fiber preform deposited at  $800^\circ\text{C}$ , which caused bottleneck effect to prevent the TEOS gas from entering into the preform, so the inside of preform had little  $\text{SiO}_2$  matrix. But, the matrix densification is very high depositing at  $750^\circ\text{C}$ , the outside and inside of the preform were all deposited at the same time. Experiment results show the optimal deposition temperature is  $750^\circ\text{C}$ . Low manufacturing temperature could minimize degradation to the Nextel 480 fiber during deposition to retain the strength of the fiber.

The conclusion of the study is Nextel 480/Silica Composite could be manufactured by APCVI. The optimal deposition temperature is  $750^\circ\text{C}$ . The thermal expansion coefficient of the amorphous  $\text{SiO}_2$  matrix matches with the Nextel 480 fiber.

## **Processing and microstructure of WHIPOX<sup>TM</sup>**

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Keywords: Oxide/oxide, Nextel 610, Nextel 720, winding technique, failure tolerance

Winded high porous oxide ceramic matrix composites (WHIPOX<sup>TM</sup>) are promising candidates for high temperature and long term applications in oxidizing atmospheres. 1D- and 2D - composites have been developed based on highly porous mullite matrices (porosity > 60 vol.% ) and various oxide fibers such as Nextel<sup>TM</sup> 610, 650 and 720 and are fabricated by a computer controlled winding technique developed at DLR.

This contribution describes the multiple shaping of WHIPOX<sup>TM</sup> realized by the special winding software CADWIND<sup>TM</sup> which can generate winding models automatically for every important mandrel geometry after entering the wanted winding parameters (e.g. winding angle, pattern number or degree of covering). To produce e.g. rings or tubes the greenbody are dried on the mandrel – prepregs are removed from the mandrel and be stacked or joined in the moist stage to realize other different shapes. The dried components are pressureless sintered in air at 1300°C.

The development of the typical laminated microstructure and the influence of the winding parameter on the fiber distribution and the fiber content (between 25 and 40 vol.%) will be presented.



## Long Fibre Reinforced Damage-tolerant Oxide/Oxide CMCs with Polysiloxanes

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**Keywords:** LPI-process, polysiloxanes, RTM, coating of fabrics, characterisation

Silicon based preceramic polymers (polysiloxanes) are attractive candidates to produce high temperature and corrosion resistant ceramic fibres, coatings and even bulk materials. Moreover, they can be used to build up a ceramic matrix in damage tolerant long fibre reinforced ceramic matrix composites (CMC) via the liquid polymer infiltration and pyrolysis route (LPI-process). The resulting amorphous glass-like silicon oxycarbide matrix is resistant to crystallization and oxidation at temperatures above 1000 °C in combination with an outstanding high temperature strength and chemical stability compared to vitreous silica. The high oxidation resistance is due to the self-protecting silica layer on the surface and the slow diffusion of gases, especially oxygen and water, into the silicon oxycarbide.



Surface of oxide/oxide CMC after welding torch test.

At DLR commercially available, economically priced polysiloxanes are used to build up a polymer silicone matrix via the resin transfer moulding technique (RTM). Therefore, polyaddition type as well as polycondensation type resins, which upon pyrolysis yield silicon oxycarbides with different chemical compositions and physical properties, were applied. The reinforcing fibres are commercially available high temperature resistant aluminosilicate fibres with an intrinsic oxidation stability, one mostly amorphous type (Nitivy) and one crystalline type consisting of mullite and alumina (Nextel 720). After infiltration of the fabrics and subsequent curing of the polymer in the mould the composite is pyrolysed at 1100 °C in nitrogen atmosphere. Due to the shrinkage of the matrix and the stiffness of the fibres the resulting open porosity in the range of 30 % after pyrolysis is reduced by 2 further infiltration steps with polysiloxanes via RTM and subsequent pyrolysis steps to about 15 %. The resulting composite, however, has a brittle fracture behaviour.

In order to overcome this problem a fugitive coating was performed. Therefore, the fabrics were coated with a phenolic resin prior to RTM-processing. After the last pyrolysis step the C-coating was burned off at 700 °C for 20 h in air yielding a definite gap around the fibres, resulting in an oxide/oxide CMC with excellent thermal shock resistance and improved fracture toughness.

In this paper the process itself as well as the mechanical, some physical and chemical properties of the oxide/oxide CMC as well as the intermediate composites are reported.

## A Low Cost Fabrication Route of All Oxide Composites: Fabrication and Mechanical Properties

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Continuous fiber ceramic composites are candidate materials for high temperature components as they have high fracture resistance, thermal shock resistance and other properties. However, the oxidation resistance of non-oxide composites is poor due to the carbon or BN interphase between fibers and the matrix. Therefore, oxide fiber reinforced oxide matrix (all-oxide) composites have been expected to be used in oxidation environment. The control of the interface between oxide fiber and oxide matrix is still not solved.

A new kind of all-oxide composite was developed which was  $\text{Al}_2\text{O}_3$  ceramics reinforced by a plane-woven minicomposite fabric consisting of  $\text{Al}_2\text{O}_3$  fiber and  $\text{ZrO}_2$  matrix. The processing of the minicomposite was that  $\text{Al}_2\text{O}_3$  fibers were dipped into a colloidal  $\text{ZrO}_2$  solution. Then the plane-woven minicomposite fabrics were infiltrated by  $\text{Al}_2\text{O}_3$  powder-dispersed slurry. Finally, the infiltrated  $\text{Al}_2\text{O}_3/\text{ZrO}_2$  minicomposite fabrics were stacked, pressed and sintered in ambient air to form a plate shape of all-oxide composite. The effect of sintering temperature on tensile strength was investigated to determine an optimum sintering temperature. The tensile stress-strain behavior and fracture resistance of the optimized composite were studied in details. The composite showed non-catastrophic fracture behavior with extensive fiber bundle unit pullouts. The ultimate tensile strength of the composite with a fiber volume fraction of 0.3 was about 70 MPa, which was 70% of the strength of the bare fiber bundle.

## **Aluminium phosphate bonded oxide fibre reinforced porous mullite based matrix composites**

**Keywords:** ceramic, composite, fibre, oxide, phosphate, mullite, Nextel

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A low temperature process was developed to make porous mullite matrix/oxide fibre composites with strong interfaces. The composite uses a porous matrix instead of weak coatings to deflect cracks from the fibres. An aqueous mullite-silica slurry was used to infiltrate two-dimensional woven preforms of alumina (N610) or alumina/mullite (N720) fibres. After presintering at 1000°C, the composite was impregnated with a phosphate binder to strengthen the mullite matrix network and fired at 1000°C again. Good matrix infiltration of fibre tows was obtained with no drying/sintering cracks apparent. Fibre volume fractions around 35-40% were reached. The mechanical properties of the composites were assessed by flexural testing. Non-brittle fracture behaviour was demonstrated and strengths of 210 MPa and 150 MPa were recorded for N610 and N720 composites respectively. The results indicate that the process did not degrade the fibre properties.

## **Oxide fibers produced by internal crystallization method and their usage in oxide-matrix composites**

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Oxide-fiber/oxide-matrix composites can be structural materials for very high temperatures, say, for temperature interval of 1200-1500°C, provided fibres of high thermal stability and high creep resistance at such temperatures are available. Single crystalline and eutectic oxide fibers grown from the melt belong to this class of the reinforcement. However, well-known methods of fiber growth such as edge defined, film-fed growth (EFG), laser heated pedestal growth (LHPG), and so called  $\mu$ -pulling-down method can be used for producing fibers only for special applications since they are certainly too expensive to be used in structural applications.

A method to produce single-crystalline and eutectic oxide fibers based on the internal crystallization, that is crystallization of the oxide melt infiltrated into continuous channels made in an auxiliary matrix, i.e. molybdenum one, and then extraction of the fibers from the auxiliary matrix by i.e. chemical dissolution of it looks a promising starting point for the development of a fabrication technology of heat-resistant structural fibers. The method developed in the authors' laboratory is relative simple and requires sufficiently small energy input into a real process. Because crystallizing a batch of the fibres by using ICM is actually similar to making bulk crystals, an expected cost of ICM fibres is of the same order of magnitudes as that of bulk crystals. The method allows obtaining a variety of oxide fibers, such as sapphire and YAG of a homogeneous crystallographic orientation, alumina-YAG eutectic, and single crystalline mullite.

In the present paper, fundamentals of the internal crystallization method (ICM), strength characteristics of oxide fibers produced by ICM, and an example of the usage of such a fiber in an oxide matrix are outlined.

# **Processing and Characterisation of Nextel<sup>TM</sup> 720 Fibre-Reinforced Mullite Matrix Composites from Hydrothermally Processed Mullite Precursors Using Electrophoretic Deposition and Pressure Filtration**

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**Keywords:** Mullite fibre, mullite, hydrothermal processing, electrophoretic deposition, composite

Continuous oxide fibre-reinforced oxide ceramic matrix composites are under development for high temperature structural applications due to their damage-tolerant behaviour resulting from the decreased flaw sensitivity and resistance to creep. The main challenge is 'how to process' such composites using cost-effective and reliable manufacturing techniques that could be competitive against well-established but expensive processing techniques, such as CVI and hot pressing.

The present work reports the development of a combined processing technique comprising in-situ electrophoretic deposition (EPD) and pressure filtration (PF) in order to produce high density mullite fibre-reinforced mullite composites. A kinetically stable and well-dispersed aqueous base mullite precursor was prepared using hydrothermally produced sinter-active (monophasic) mullite+5 wt % zirconia powders. Woven Nextel<sup>TM</sup> 720 mullite fibres were coated with laboratory prepared NdPO<sub>4</sub> or zirconia using dip-coating. Coated fibre mats were then used in an in-situ EPD cell as deposition electrode in order to infiltrate the very tight inter/intra fibre tow regions with the nano-size mullite particles. Finally, eight layers of infiltrated fibre preforms were placed in a high load pressure filtration assembly, leading to formation of consolidated compacts with high green densities. After sintering at 1250°C for 2 h, the compacts had a density of 86.4 % of theoretical density. The mechanical properties of composite samples were determined, and the effects of the interphase materials on the thermomechanical properties of the final component are discussed in terms of the damage-tolerant behaviour and toughening achieved. The present work demonstrates that woven mullite fibre-reinforced mullite matrix composites can be processed by a simple method, involving single stage EPD and PF infiltration followed by pressureless sintering.

## **Microfabrication of Damage-Tolerant $\text{Al}_2\text{O}_3/\text{ZrO}_2$ Fibril Composites via Aligned Bi-phase Microlaminae Using Co-Extrusion**

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**Keywords:** Fibril composites, alumina, zirconia, co-extrusion, interface

The efficiency and quality of emissions of gas turbines used in aero-engines and ground based energy production as well as the production of glasses and similar materials at high temperatures are limited by the upper temperature limits of metal alloys. Although monolithic ceramics are stable at higher temperatures, their low fracture strength and toughness as well as thermal shock resistance make them weak candidate for such application. Fibre-reinforced ceramic composites are very expensive to produce and cannot be used over 1200°C due to instability of the fibres at higher temperatures. The work presented here addresses both of these problems and offers a cheap, rapid and effective means of producing a new family of structural materials capable of operating up to 1400°C, in air and without cooling.

The proposed material was developed and produced by sol-based technology which involves the extrusion, at room temperature, of a two phase material resulting in an aligned bi-phase structure which was then be re-extruded to reduce the widths of the phases. Each monofilament was coated with zirconia or  $\text{NdPO}_4$  using dip-coating in order to create oriented weak interphase. These coated filaments were then positioned together in a mould where the structure are consolidated and sintered to form a multi-phase composite material. The process allows the microstructure to be controlled at a nano-meter scale within each extruded filament. All the critical steps in the preparation of nano-size alumina and zirconia sols and the rheological behaviour of the two dissimilar sol-gel derived pastes (alumina and zirconia) are described. Room and high temperature mechanical behaviour of the monofilaments and multiple co-extruded component were correlated with the microstructural features.

## **Modelling the co-extrusion of ceramic pastes for fabrication of fibrous monolithic composites**

I. Aldazabal, J. Flaquer, J.M. Martínez-Esnaola and J. Gil Sevillano, Centro de Estudios e Investigaciones Técnicas de Gipuzkoa (CEIT), San Sebastián, Spain.

Keywords: Oxide/oxide CMC, co-extrusion, pastes, modelling, fibre.

The co-extrusion of mixtures of two different concentrated ceramic suspensions has been modelled for simulating the fabrication of fibrous two-phase monoliths of alternating ceramic fibres. A Krieger-Dougherty constitutive behaviour is assumed for the pastes with allowance for shear-thinning. The deforming section or volume is discretised in triangular or tetrahedral elements for respectively 2-d or 3-d simulations. For each strain increment the displacement field is modified using a Monte Carlo procedure with annealing until the energy spent in the deformation step is minimised. Liquid migration in the deforming zone is allowed to occur assuming perfect permeability. The simulations provide information on the shape retention of the section of the fibres and on the distribution of the fraction of solids in the final compact, as a function of the deformation geometry and the relative behaviour of the pastes.

## **Dispersion and Rheological Characteristics of Silicon Carbide Whisker in Mullite Slurry**

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Silicon Carbide whisker dispersing behavior in Mullite slurry was study by sedimentation and rheological measuring. The effect of PH value and dispersant on dispersion of SiC whiskers were discussed. The results shows that whiskers added were seriously affect the rheological properties of slurry. When PH=11 and dispersant content 5wt%, uniform dispersion slurry can be obtained. Using this dispersion process, we can get uniformity structure of SiC whisker reinforced Mullite composite after sintering



## Optical and Mechanical Behavior of Woven Fabric $\text{Al}_2\text{O}_3$ Fiber-Reinforced $\text{MgAl}_2\text{O}_4$ Matrix All-Oxide Optomechanical Composites

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Keywords: Optically transparent  $\text{MgAl}_2\text{O}_4$ , optomechanical composite, in-situ observation

Recently, several oxide and non-oxide optically transparent ceramics became available for applications that require high optical transmission together with high strength and hardness at elevated temperatures. High temperature monitoring window can be given as a typical example to these applications. Nevertheless, low fracture resistance of optically transparent ceramics under the service conditions limits their applicability although their usage can considerably simplify the design of the overall structure.

To overcome this limitation, optically transparent ceramics were reinforced with continuous ceramic fibers in order to form light transmitting optomechanical composites for high temperature monitoring window application, which was proposed by the present authors. In a previous study, this idea was applied to SiC fiber-reinforced magnesium aluminate spinel matrix ( $\text{MgAl}_2\text{O}_4$ ) optomechanical composites.  $\text{MgAl}_2\text{O}_4$  was chosen as the matrix material because of its isotropic optical properties due to the spinel structure, high temperature strength and chemical inertness to alkalis and oxidation. Since in that study the fiber/matrix interfacial area, which causes light scattering losses, was aimed to be minimized by the regular arrangement of the fibers in the matrix, thick SiC (SCS-6) fiber was chosen as the reinforcing second phase. However, the large thermal expansion coefficient mismatch between the fiber and the matrix caused fabrication difficulties in terms of increasing number of fiber layers in the matrix. Despite these difficulties, fabricated optomechanical composites containing a single layer of unidirectionally aligned SiC fibers revealed considerable light transmittance together with a fail-safe mechanism in which the intact fibers bridge the matrix crack after it passed through the whole width of the composite.

In the present study,  $\text{MgAl}_2\text{O}_4$  matrix was reinforced by  $\text{Al}_2\text{O}_3$ -fiber bundle  $\text{ZrO}_2$  matrix minicomposite because of the closer thermal expansion coefficient matching between  $\text{Al}_2\text{O}_3$  fiber and  $\text{MgAl}_2\text{O}_4$  matrix. After a number of bundles were removed from the  $\text{Al}_2\text{O}_3$  plain woven fabric to create a 0-90° fiber-bundle mesh like structure with openings that allow light passage through the resulting composite, it was coated by colloidal  $\text{ZrO}_2$  to prevent its interaction with the matrix phase under the processing conditions. Finally, all-oxide light transmitting optomechanical composite was fabricated by hot-pressing followed by HIPing.

The usage of  $\text{Al}_2\text{O}_3$ -fiber bundle was effective in eliminating fabrication difficulties that result from the thermal expansion coefficient mismatch between the fiber and the matrix. Additionally,  $\text{ZrO}_2$  coating on the  $\text{Al}_2\text{O}_3$ -fiber bundle was used to avoid the dissolution of the fiber in the matrix phase under the applied processing condition. Fabricated composite revealed considerable amount of light transmission by the usage of optical window, which is defined as the optically transparent regions of the matrix that is surrounded by the incorporated fibers. The direct observation of the fabricated composites under a scanning electron microscope using a specially designed testing fixture clearly demonstrated the effect of fiber on the crack growth resistance of the composite.

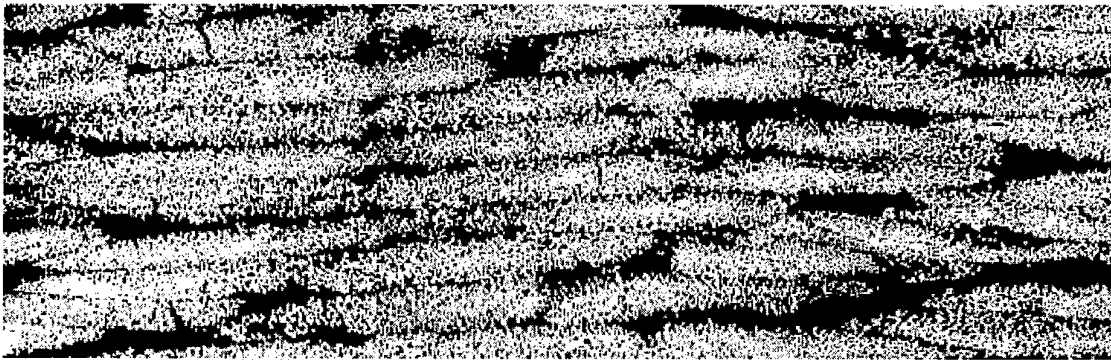
Topic: (D) Oxide/Oxide CMCs

## Mesostructure of WHIPOX<sup>TM</sup> all oxide ceramics

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Keywords: characterization, fiber distribution, Whipox CMC

WHIPOX<sup>TM</sup> all oxide ceramics consist of alumina or aluminosilicate fibers (e.g. Nextel 610, Nextel 720) and a highly porous mullite matrix. In the ideal case, both, the fiber distribution and the (sub)micro-scale matrix porosity is uniform. In reality, however, flaws ranging from microscopic to mesoscopic do exist with pertinance to the material's properties. Most important flaws occurring in Whipox composites are voids up to 100  $\mu\text{m}$  in diameter and non-uniform fiber distribution, the latter leading to relatively large fiber-free areas. These effects are due to the fabrication process that makes use of fiber rovings infiltrated by a matrix slurry and subsequent winding, shaping and firing. Characterization and quantification of the flaws is essential for optimization of the composite processing and is fundamental for future materials modelling.



1.5mm x 5mm section of Whipox showing fiber clusters and fiber-free areas.

Whipox composites were fabricated under reproducible conditions and tested mechanically by 3-point bending. The fabrication-induced flaws were analyzed by optical microscopy in a combination of transmission and reflection mode using polished thick sections. Ceramographic sample preparation of the porous material was enabled by infiltration with a low-viscous epoxy resin. Analysis of intrabundle fiber distribution and quantification of fiber-free areas was performed in the transmission mode making use of the fibers' light conduction. Mesoscopic pores, on the other hand, were registered by reflected light. Up to 24 electronical micrographs per section were recorded to characterize the cross section of the sample entirely. Image processing and analysis was performed using a personal computer. The intrabundle fiber distribution was analyzed by two different techniques: On the one hand, the distribution of nearest fiber-fiber distances was determined. On the other hand, cells around the fibers centroids were constructed which include all points closer to a selected fiber than to any other and subsequently the size distribution of the cells was established.

The investigations reveal that the roving dimensions, i.e. the number of filaments per roving have strong influence on the mesostructure of the composite.

## Mechanical Behavior of WHIPOX<sup>TM</sup>– CMC's with Nextel 610, 650 and 720 Fibers

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Keywords: Ceramic; Composites; Oxide; Nextel; Mechanical Properties; WHIPOX

Winded high porous oxide ceramic matrix composites (WHIPOX-CMC's) are promising candidates for high temperature and long term applications in oxidizing atmospheres. In this study the strength and damage behavior, the thermal stability, the high temperature deformation behavior and the time dependent damage of the oxide fibers (Nextel 610, 650 and 720) and of the WHIPOX-CMC's was investigated. Dependent on the winding angle and the loading directions the strength of the composites ranges between 70 and 300 MPa.

The table shows the critical temperatures  $T_c$  for long term applications under mechanical loading for the various fiber types and for the WHIPOX –CMC's.

	$T_c$ (Fibers)	$T_c$ (WHIPOX-CMC's)
Nextel 610	800°C	800-850°C
Nextel 650	850-900°C	850°C
Nextel 720	1000°C	1000°C

Caused by the high matrix porosity (up to 80 vol.%), the mechanical behavior of the composites is mainly controlled by the fiber properties. For long term applications at temperatures up to 900°C the alumina rich fiber types Nextel 610 or 650 may be used to fabricate the WHIPOX-CMC's due to their favorable strength. For higher temperature applications (1000°C or more) the alumino silicate fiber Nextel 720 is more suitable for composites where long term stability is required.

During cyclic fatigue testing at room temperature and 1000°C all composites show no fatigue effects up to stresses near to fracture strength. In burner tests with very hard thermal shock conditions WHIPOX-CMC's display no damage below the melting point of composites.

Beside the intrinsic oxidation stability, WHIPOX-CMC's exhibit sufficient strength for many technical applications, a non brittle fracture behavior, an excellent thermal shock resistance and a good stability against cyclic loading.

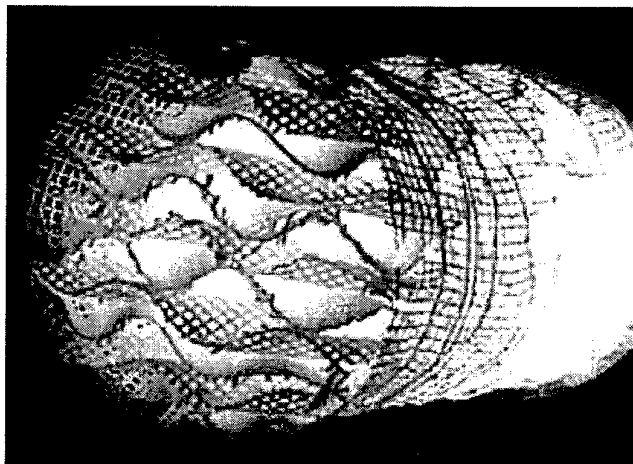
## **“KERAMIKBLECH” PROPERTIES AND APPLICATIONS**

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Keywords: oxide/oxide CMCs, high temperature applications, thinwalled lightweight structures

“Keramiklech” / “sheet ceramic” is an oxide fibre reinforced oxide ceramic developed and produced by the company Walter E.C. Pritzkow Spezialkeramik. The different types of “Keramiklech” are based on glass or ceramic endless fibres and matrix materials based on  $\text{SiO}_2$ , mullit and or  $\text{Al}_2\text{O}_3$ . Bending strength of up to  $180 \text{ N/mm}^2$  is reached. The materials are used in oxidizing atmosphere up to  $1730^\circ\text{C}$  mainly as follows:

- thinwalled light weight structures (0,3-5 mm)
- thermal mechanical loaded structures
- thermal chemical loaded structures
- thermal shock resistant and damage tolerant constructions



open porous medium burner made of perforated sheet ceramic

The applications are:

- static mixers for burner technologies made of perforated sheet ceramic (see figure)
- setter plates for kilns used in the sinter metal production and the ceramic industry up to temperatures of  $1730^\circ\text{C}$
- chimney tubes made of a low cost material
- parts for the aluminum casting with special coatings
- replacements for metal structures in applications with high corrosion and high temperatures
- support structures for high temperature solar absorbers

## **Long term properties of ceramic matrix composites under high temperature mechanical loading**

Dietmar Koch, Georg Grathwohl, Keramische Werkstoffe und Bauteile, Universität Bremen, Germany

Keywords: oxide/oxide composites, non oxide composites, creep, reinforcement, interphases, application

Ceramic matrix composites are mainly developed as structural components for high temperature applications under ambient or inert atmosphere. In this paper the high temperature properties of different composite systems are investigated in order to determine the limits of temperature and applied stresses when these materials are used under long term conditions.

SiC/Al<sub>2</sub>O<sub>3</sub> composites consisting of HiNicalon fibers and alumina matrix processed by melt infiltration and reaction are tested at moderate (900°C) and high (1300°C) temperatures under tensile creep conditions. This oxide matrix could be considered as being "intrinsically" oxidation resistant if the oxide matrix would be able to protect the fibers and fiber/matrix interphase against oxidation. However, the results show that this protection is not effective at 900°C and no passivation can be reached, as the carbon containing fiber/matrix interphase oxidizes leading to an embrittlement of the composite which results in a low failure strain and premature failure. At even higher temperatures the matrix is very susceptible to creep and the creep behavior of the composite is dominated by the fibers. High strains to failure are achieved at stress levels of about 50% of the high temperature strength. The effects of the changing interface between fiber and matrix during high temperature loading are investigated by push-in tests and the rupture of the macroscopic bodies can be interpreted by the results of these micromechanical tests.

C/SiC composites which are very sensitive to oxidation are mainly applied at inert conditions or they are used after being coated with oxidation protection layers. Thus, the limit properties of these nonoxide composites are to be measured under argon atmosphere. It turns out that under various loading conditions as bending, compression, tension and creep the maximum applicable temperature is well above the one observed for SiC/Al<sub>2</sub>O<sub>3</sub> composites. The limiting component is the matrix which governs the intra- and interlaminar stability of the composite. This fact is of particular importance for bidirectionally reinforced materials and multiaxial loading conditions. The fractional parts of the fibers and the matrix, respectively, on the creep behavior of the composite is evaluated by creep tests under tensile and bending loading conditions.

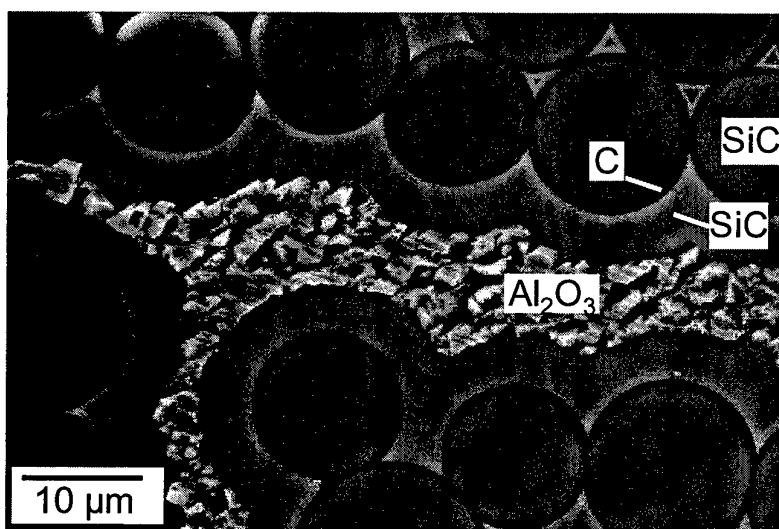
## Oxidation behaviour of a fibre reinforced $\text{SiC}_{(f)}/\text{Al}_2\text{O}_3$ composite

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Institut für Keramik im Maschinenbau, Universität Karlsruhe, Germany

Keywords: oxidation, mechanical properties, indentation test, fibre matrix strength

Ceramic Matrix Composites (CMC) may be used as heat protection tiles in combustion-chambers. In this background the cyclic oxidation behaviour and the effect on mechanical properties of a  $\text{SiC}$ -fibre reinforced alumina-matrix composite has been tested up to temperatures of 1400 C and 1000 hours resp.. The cyclic oxidation tests were performed by heating in a vertical tube furnace and cooling down from maximum temperature by compressed air. The strength degradation after cyclic oxidation treatment is discussed in context with microstructural features of the composite materials.



Microstructure of the  $\text{SiC}_{(f)}/\text{Al}_2\text{O}_3$  composite tested.

During oxidation of this composite material several reactions which can lead to mass decrease and mass increase have to be taken into account. These reactions greatly influence the mechanical behaviour of the composite. Especially important is the alteration of the fibre-matrix interface. Push-in tests with an indenter showed an increasing interface bonding leading to fracture of the fibres without pull-out. At high temperatures mullite is formed, which leads to cracks and increased oxidative attack. This effect and the fibre degradation is manifested in substantially reduced strength.

# **Effect of Notches, Specimen Size, and Fiber Orientation on the Monotonic Tensile Behavior of Oxide-Oxide Composites at Ambient and Elevated Temperatures**

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The effect of circular center holes on the monotonic tensile stress-strain behavior and strength of a continuous fiber-reinforced oxide/oxide composite was investigated at ambient and elevated temperatures. The material used in this study consisted of 12 layers of un-coated plain weave fabric of Nextel™ 720, with either 0/90 or  $\pm 45^\circ$  fiber orientation with respect to the loading direction, and an aluminosilicate matrix.

100 and 200-mm long straight-sided specimens with center holes were tested for ratios of hole diameter to width ( $a/w$ ) between 0.1 and 0.4, and width values between 3 mm and 25 mm. It was found that as-processed specimens with both fiber architectures were notch insensitive at ambient temperature, but exhibited mild notch sensitivity at elevated temperatures. It was also found that the strength of the material was retained after heat treatments at 1000°C, but that it decreased significantly after exposures at 1100°C for periods of time of 20 and 100 hours. The strength of test specimens with 0/90 fiber orientation was found to decrease with increasing width, but no size effects on strength were observed for specimens with  $\pm 45^\circ$  fiber orientations. These results are discussed in relation to the microstructure of the material and its evolution at elevated temperatures.

**KEYWORDS:** ceramic matrix composite, oxide/oxide, notch, notch sensitivity, strength, size effects, fiber orientation, high temperature

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## High Temperature Strength of Directionally-Solidified $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{Y}_2\text{O}_3)$ Eutectics

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Keywords: Eutectic oxides; high temperature strength; fracture micromechanisms.

Eutectic crystals grown from the melt constitute a family of *in situ* composites with a fine microstructure and an excellent bonding between the phases. In addition, the phases in the eutectic are thermodynamically compatible up to temperatures approaching the eutectic temperature, which opens great possibilities for high temperature applications, particularly in the case of eutectic ceramic oxides, where each phase is also chemically stable in oxidizing environments even at very high temperatures.

The mechanical properties of  $\text{Al}_2\text{O}_3\text{-ZrO}_2(\text{Y}_2\text{O}_3)$  up to 1700 K are studied in this paper. The composites were produced by directional solidification using the laser-heated float zone method, and its microstructure was mainly formed by colonies consisting of a fine network of  $\text{ZrO}_2$  and  $\gamma$ - $\text{Al}_2\text{O}_3$ . The colonies (transverse diameter  $\sim 31 \pm 10 \text{ } \mu\text{m}$ ) were elongated in the growth direction. The composite samples exhibited an average flexure strength over 1.1 GPa at ambient temperature, which was a result of the combination of the high toughness (7.8 MPavm) with a small critical defect size. The flexure strength of the composite was determined at 1300, 1500 and 1700 K. The excellent mechanical properties in the longitudinal direction were maintained up to 1700 K, where average flexure strengths in excess of 800 MPa were measured. This behavior is significantly better than that of either monolithic ceramics ( $\text{Si}_3\text{N}_4$ , SiC) or whisker- and fiber-reinforced ceramic composites at the same temperature. In addition, it was shown that the eutectic microstructure was stable after one hour at 1700 K.

The fracture micromechanisms at ambient and elevated temperature were analyzed under the scanning electron microscope. It was shown that fracture was initiated in surface defects associated with pores and longitudinal cracks at the colony boundaries. The area of these defects was much larger perpendicularly to the transverse direction, and thus the transverse tensile strength was more than one order of magnitude lower than the longitudinal one. No changes in the fracture initiation loci were found in samples tested at high temperature and the origin of the strength reduction was very likely associated to the drop in the eutectic oxide toughness caused by the release of the thermal residual stresses.



## CERAMIC COMPOSITES $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{MgO}$

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The progress of modern techniques requires new reinforcing thermal-resistant and corrosion-proof ceramic materials be used. In particular, a composite  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{Me}_x\text{O}_y$  is one of the promising materials. High disperse powders and fibres are utilised for production of ceramics with good mechanical properties.

The present communication deals both with the problems on fabricating composites from fibrous  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{MgO}$  powders or aluminium hydroxide gel with partial stabilised zirconia fibres, and with the influences of a composition and preparing methods on a structure and properties of ceramics.

The composites were prepared in two ways: by precipitation of aluminium hydrated gel with partial stabilised zirconia fibrous powder. Then the precipitates were washed, dried, moulded and heat-treated in air between 100 and 1600°C. The ceramics were also prepared from fibrous  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{MgO}$  powders using classic ceramic technology.

The investigations of oxide structure and phase transformations were performed by XRD (DRON-3 powder diffractometer,  $\text{CuK}_\alpha$  radiation, Ni filter. Specific surface areas of samples were determined by BET method, and their morphology was examined on an electron microscope (JEOL ISM-35C). A dehydration process of aluminium hydrated gel and its composites with fibres was investigated by thermal analysis. Chemical resistance of ceramics was estimated in acid, alkaline, and neutral solutions. Mechanical properties were determined by standard methods.

The influence of zirconia fibres on aluminium hydroxide gel dehydration and on  $\gamma$ -alumina crystallisation is established. During gel formation and heat treatment of precipitates physicochemical interaction occurred between zirconia fibres and colloidal particles of aluminium hydroxide. As a result, a matrix of the composite material with  $\text{ZrO}_2$  ( $\text{MgO}$ ) fibres was not crystallised up to 700°C, while the fibres had a mixture of tetragonal and monoclinic modifications. Over the temperature range 800-1000°C alumina existed in two phases:  $\gamma$  and  $\theta$ , at 1100°C they transformed into  $\alpha$ -corundum. At above 1100°C heat treatment the fibrous  $\text{ZrO}_2$  solid solution was partially destroyed, and magnesia interacted with alumina to form spinel at the matrix-fibres boundary. As a result, a heterogeneous system was formed and the material integrity was preserved. While producing from fibrous  $\text{Al}_2\text{O}_3 - \text{ZrO}_2 - \text{MgO}$  powders an addition of magnesia was not enough to stabilise a tetragonal  $\text{ZrO}_2$  structure. Never the less, this structure was formed and then preserved up to 1600°C. Over the range 1200-1250°C the solid solution of zirconia partially destroyed and spinel was formed.

The problems of physicochemical interaction during production of composite materials with alumina matrix reinforced by ceramic fibres and also of the influence of preparing methods were discussed.

## Creep Behavior of In-situ Single Crystal Oxide Ceramics Eutectic Composites in Ultra-high Temperature, High Pressure and Moisture Rich Environments

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Recently, in-situ single crystal oxide ceramics eutectic composites,  $\text{Al}_2\text{O}_3/\text{Y}_3\text{Al}_5\text{O}_{12}$  (YAG),  $\text{Al}_2\text{O}_3/\text{GdAlO}_3$  (GAP) and  $\text{Al}_2\text{O}_3/\text{Er}_3\text{Al}_5\text{O}_{12}$  (EAG) have been researched and developed. They are generally considered to be one of the most interesting and attractive as the ultra-high temperature structural materials in the field of aeronautics, aerospace and power generator industries. They have many potentialities that the tensile strength is maintained right below the melting point temperature, increases with decreasing of a characteristic dimension of the network microstructure without the reduction of creep resistance and plastically deformed at ultra-high temperature ranges. Also, there is a good productivity of complex structural components as compared with conventional sintered engineering ceramics. However very low fracture toughness and thermal shock resistance originally resulted from the oxide/oxide composite are critical problems. We had already reported both fracture toughness and fatigue crack growth resistance.

This paper focuses on tensile creep behavior of  $\text{Al}_2\text{O}_3/\text{YAG}$  and  $\text{Al}_2\text{O}_3/\text{YAG}/\text{ZrO}_2$  eutectic composites in ultra-high temperature over  $1500^\circ\text{C}$ , high pressure and moisture rich environments. There is a quite difference between tensile and compressive creep behavior and tensile creep has a poor resistance as compared with that of compressive creep. There is also a remarkable influence of high pressure, moisture rich environments which are accelerated the tensile creep deformation rates and environmental degradations. Finally, creep deformation rates are compared with other typical high temperature structural materials, that is, super-alloys, intermetallic compounds, monolithic ceramics and ceramic matrix composites.

**Acknowledgements:** This research had been conducted as a part of feasibility studies on application to  $1700^\circ\text{C}$  class non-cooled, TBC-free high efficient turbine system in New Sunshine Program of Agency of Industrial Science and Technology, MITI.

## Microstructure Design Concepts for Damage Tolerance Behavior in Alumina/Alumina Laminate Composites

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Alumina/alumina laminate composite is one of the promising candidates mainly due to high oxidation stability at high temperature application. The key factor for the achievement of alumina/alumina laminate composite is to provide weak interface for damage tolerance behavior. This depends upon the microstructure of interface for effective crack deflection. In this study, two-microstructure design concepts have been suggested for the damage tolerance behavior of alumina/alumina laminate composites. One is the porous/dense alumina laminate composite using pore orientation parallel to the interface. Pore orientated alumina layer was fabricated by the control of graphite dispersion and burnout process. The other is the in situ co-textured alumina laminate composite composed of alumina and Ca-hexaluminate ( $\text{CA}_6$ ). In situ co-textured microstructure was fabricated using alumina platelet and monticellite. Cracks, generated by Vickers indentation, were deflected at the interface of porous/dense layer and also propagated with stepped manner in porous layer. In co-textured alumina laminate composites, indentation pattern showed a diffused damage pattern due to crack shielding effect resulted from weak interface. When the cracks entered into the co-textured layer, cracks were deflected at the interface between  $\text{CA}_6$  and alumina, and also crack bridging was observed.

## Mechanical Properties of Si-Ti-C-O fabric/polytitanocarbosilane/mullite Laminate Composites

Y. Nakamura\*, S. Kasuga\*, J. Nakamura\*\*<sup>1)</sup> and Y. Hirata\*\*, \*Department of Mechanical Engineering, \*\*Department of Applied Chemistry and Chemical Engineering, Kagoshima University, 1-21-40 Korimoto, Kagoshima 890-0065, Japan.

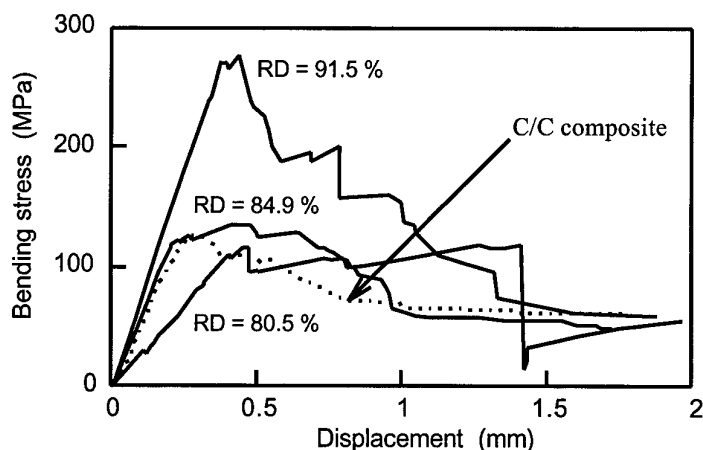
1) Now at Kyocera, Co., 1-1 Yamashita-cho, Kokubu-Shi, Kagoshima 899-4396, Japan.

**Keywords:** Si-Ti-C-O fabric, polytitanocarbosilane, mullite, nonlinear fracture

High fracture resistance is one of the most important properties required for high-temperature-structural CMCs. Laminates composed of the Si-Ti-C-O fabric and mullite matrix as a CMC system are expected to show high fracture resistance. However, it is preferred to fabricate the laminate composites by using materials with more similar properties in order to suppress the formation of large residual stresses which arise from the difference in thermal expansion and elastic behaviors. Polytitanocarbosilane (PTC) is known as a precursor of Si-Ti-C-O fiber. Thus, incorporating the infiltration and pyrolysis of PTC into the synthesis of Si-Ti-C-O fabric/mullite composites is expected to give more Si-Ti-C-O-like matrix by the decomposition of PTC. On the other hand, a large number of pores remain in the matrix, which are considered to affect the mechanical properties of the composites.

The present study reports mechanical properties of Si-Ti-C-O fabric/PTC/mullite laminate composites examined as a function of the relative density. A PTC/xylene solution was infiltrated into the spaces of laminated, porous Si-Ti-C-O fabric/mullite sheets, and pyrolyzed at a temperature of 1273 K. The resultant composites have relative densities ranging from 80.5 % to 91.5 % according to the number of the infiltration/pyrolysis routes. Four-point-bend-testing shows that the composites deform nonlinearly, and do not fail completely, as shown in Fig.1. The flexural strength increases with increasing the relative density, and the work of deformation to a displacement of 1.6 mm is 9.7 – 21.2 kJ m<sup>-2</sup>, which is comparable to or larger than that of C/C composites. The composites also exhibit nonlinear fracture in shearing-tests conducted in a direction parallel to the sheets. The shear strength increases with increasing the relative density. The pseudoplasticity of the composites is attributed to the delamination of the sheets as well as the pulling-out of Si-Ti-C-O fibers on crack propagation in the fabrics.

Fig.1. Bending stress-displacement curves of Si-Ti-C-O fabric/PTC/mullite laminate composites. RD; relative density.



# **Fibers**

**Monday, October 1<sup>st</sup>**  
**Afternoon session**

## Behaviors of Polymer-Derived SiC Fibers under Several Environments

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Keywords: SiC fiber, Polycarbosilane, CMC, Oxidation, Creep

SiC-based fibers have been gradually used as reinforcements of ceramic matrix composite (CMC). They have been mainly produced from polycarbosilane (PCS) of organosilicon polymer, and are flexible fibers with a diameter of 12-14mm. The first fiber fabricated has nano-scale microstructure, next, low-oxygen contained fiber was developed, and finally, sintered fiber has been created. These fibers are called Nicalon, HI-Nicalon, and HI-Nicalon-S, respectively. Nicalon is thermodynamically unstable at high temperature and is composed of nanometetric crystals (about 2nm) of b-SiC, free carbon and amorphous silicon oxycarbide phase (SiOxCy). HI-Nicalon exhibits better thermal stability than Nicalon and consists of b-SiC nanocrystals (about 5nm), free carbon and a small amount of SiOxCy. HI-Nicalon-S is b-SiC sintered fibers and has excellent high-temperature resistance. The thermal stability of these fibers is considered to be owing to the amorphous SiOxCy phase and free carbon. At elevated temperatures, the amorphous SiOxCy phase thermally decomposes, and tends to crystallize into b-SiC with the generation of SiO and CO gases. These behaviors occur even in oxidizing environments. The oxidation behaviors of PCS-derived SiC fibers have already been investigated under one atmosphere of oxygen or air pressure. The behaviors of Nicalon and HI-Nicalon heat-treated at high temperatures in oxygen partial pressures or in lower pressures have been gradually studied in relation to the thermal decomposition of the amorphous SiOxCy phase.

For the present work, Nicalon, HI-Nicalon, and HI-Nicalon-S were oxidized at 1773 K under Ar-O<sub>2</sub> gas mixtures in the range of oxygen partial pressures from 102 to 105 Pa and at 1473-1773 K in low pressure of 1 Pa. Oxidation behaviors of these fibers have been studied, and further, creep behaviors of HI-Nicalon and HI-Nicalon-S at 1573-1723 K under a stream of Ar and air have been investigated. It is important to understand creep properties of these fibers as reinforcement for CMC. In this paper, the thermal stability of these PCS-derived SiC fibers is discussed on the base of experimental results of oxidation and creep behaviors.

## **New High Temperature Oxide Fibers**

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Oxide fibers have historically had poor high temperature structural capability in comparison with SiC-based fibers. However, during the last decade, oxide fibers such as Nextel™ 720 Ceramic Oxide Fibers and Nextel 650 fiber have been developed with good strength and long-term creep resistance at temperatures as high as 1100°C. Superior high temperature structural properties result from the presence of crystalline, creep-resistant phases such as  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and mullite, and the absence of amorphous phases that promote deformation at high temperature. These and other microstructure and compositional effects that generate good high temperature performance in existing oxide fibers will be discussed.

Future developments in high temperature oxide fibers are focusing on two new classes of fibers, one based on mullite, and one based on yttrium aluminum garnet. Experimental fibers at 3M and elsewhere have demonstrated that significant improvements over the properties of Nextel™ 720 fibers are possible in both classes of fiber. Properties and microstructures of advanced oxide fibers, and future prospects for oxide fibers for composite reinforcements above 1100°C, will be discussed.

## **A Low Cost and Unique Carbon Fiber for CMC**

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Keywords: CMC, C-Fibers, SiC Composites

The most advanced CMC consists of a carbon/graphite fiber in a silicon carbide matrix. The carbon fiber is a commercial PAN or pitch based production fiber without distinguishing features. A new low cost process has been developed for producing carbon/graphite fibers from a pitch precursor. One of the more costly steps in carbon fiber production is the stabilization/oxidation step that is necessary to prevent melting and interfiber fusion as pyrolysis progresses. The new process purifies the precursor pitch that includes processing which eliminates the requirement of stabilization/oxidation prior to pyrolysis/carbonization. Microwave pyrolysis/carbonization of the green fiber has been demonstrated. The pitch precursor processing is adjusted to produce an isotropic fiber or anisotropic from a mesophase than can be readily graphitized. Both solid and hollow fibers have been produced with strengths up to 4.2 GPa. A commercial demonstration line to produce these carbon/graphite fibers is scheduled for completion in 2001. The projected fiber cost is under \$12/kg. These fibers have been utilized to produce SiC and other type matrix composites. The hollow carbon fiber results in very lightweight composites.



## **The Formation Mechanism of the Stabilized Microstructure in the Fibers of $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$ System**

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Keywords: alumina, mullite, sol, framework

The short fibers of  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system were produced by sol-gel technology from the spinning solution in which  $\text{Al}_2(\text{OH})_5\text{Cl}$  was the  $\text{Al}_2\text{O}_3$  precursor and  $\text{SiO}_2$  was the structure stabilizing and sintering component.

The investigations of the fiber's fine structure showed, that the particles of  $\text{SiO}_2$ -sol kept their morphology (spheres  $\sim 20$  nm in diameter) till transformation to mullite had occurred and the latter inherited their form.

The mullite spatial framework, in which the residual  $\alpha(\delta)$ - $\text{Al}_2\text{O}_3$  stuffed pores inside, providing thereby the mutual phase stability, was formed.

The formation mechanism of the stabilized microstructure is proposed in the paper.

## POLYCOMPONENT ALUMINA-BASED FIBRES

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Inorganic fibres may be used as a filler of composites and also as initial materials to produce ceramics. Information about formation of high-temperature fibres and their structural transitions is necessary to regulate the technology of composite materials and to predict their properties.

The aim of the present work was to investigate the mechanism of forming bi-component fibres  $\text{Al}_2\text{O}_3$  -  $\text{MgO}$  and polycomponent fibres  $\text{Al}_2\text{O}_3$  -  $\text{ZrO}_2$  -  $\text{MgO}$  with different oxide ratios, and also it was our task to find a correlation between a composition, heat treatment temperature and crystal structure, and properties of fibres.

Initial materials were hydrated cellulose fibres and tissues impregnated with mixed solutions of aluminium and magnesium salts with a variable ratio from 99.5:0.5 to 35:65 mol.% in terms of metal oxides (in the case of bi-component fibres). For polycomponent fibres to be prepared impregnating solutions contained aluminium, magnesium chlorides and zirconium oxychloride in the ratio: (87,5-98,5) : (0.5-2.5) : (1-10) mol. % in terms of MeO. Polymer salt-containing fibres were thermally treated within a special regime from 100 to 1600°C. For crystal and porous structures to be studied, the X-ray methods, IR spectroscopy, the BET method were adopted. Morphological investigations of a fibre surface were made using a scanning electron microscope.

Study of the process of producing fibrous spinel is of scientific interest from the standpoint of a possible synthesis of  $\text{MgAl}_2\text{O}_4$  uniformly distributed in long objects and of practical interest for production of a component of high-temperature composites and ceramics. The conducted investigations made it possible to establish the correlation between amount of aluminium and magnesium oxides in fibres, temperature of their heat treatment and spinel formation, structural changes of aluminium oxide, as well as physicochemical characteristics of fibrous spinel. The dependence is non-monotonous in nature.

The optimum relations between components and temperature ranges of heat treatment are found. These can be obtained by controlling products with given properties: reactive fibrous filler with a high adhesive ability to a matrix or a stiff reinforcing component for high-temperature composite materials.

As a result of polycomponent fibre studies, it was found that over a temperature range of 600-1200°C the solid tetragonal solution of  $\text{ZrO}_2$  -  $\text{MgO}$  and alumina existed. Above 1200°C alumina was transformed from  $\theta$ - and  $\delta$ - phases to  $\alpha$ -corundum. High-dispersion  $\text{Al}_2\text{O}_3$  interacted with  $\text{MgO}$ , the solid solution was destroyed. So, the heterogeneous system was arranged and was composed of  $\alpha$ - $\text{Al}_2\text{O}_3$ , monoclinic  $\text{ZrO}_2$ , tetragonal  $\text{ZrO}_2$  admixture and spinel  $\text{MgAl}_2\text{O}_4$ . In all cases the fibrous architecture was safe.

## **High-Performance Si-N-O Fibres for HT-Insulation and Short-Fibre Reinforced HT-CMC's**

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Keywords: fibre, preform, CMC, MMC, insulation

Amorphous silicon oxynitride fibres (Si-N-O) have been shown to possess extraordinary high-temperature properties. They are chemically, mechanically and structurally stable up to 1400°C in nitrogen and 1200°C in air. Pilot-scale production of discontinuous fibre mats is performed by a single-step process route running at 1450°C with SiO<sub>2</sub>, SiC, Ti powder and NH<sub>3</sub> gas as inexpensive raw materials. Due to their as-processed morphology and properties, high-temperature applications focus on use of fibre preforms as filters and insulation or for reinforcement material in short-fibre reinforced CMC's and MMC's.

Fibre preforms can be produced via dispersion of the as-processed Si-N-O fibre mats in water. A binder or additive to stabilise the dried fibre preform is not necessary; however, wax is used as a binder for compressed preforms. An in-house study at EMPA was dedicated to aluminium melt infiltration of Si-N-O fibre preforms by squeeze casting method. This investigation revealed good wettability behaviour and chemical inertness of the fibres in the absence of surface-modifying coatings. This fibre/matrix interface feature facilitates good infiltration and hence prove the possibility for fibre application in short-fibre reinforced MMC's.

Industrial project partners and future users tested Si-N-O fibre preforms for fabrication of short-fibre reinforced CMC's, either by direct vapour infiltration of SiC or previous carbon infiltration with subsequent SiC infiltration. Furthermore embedding of the fibres in a RBSN was successfully performed, whereas the fibres are partially attacked by a SiSiC matrix. By these investigations could be shown that the amorphous Si-N-O fibres withstand the processing conditions without deterioration of their properties and thus represent a promising candidate for short-fibre reinforcement of high performance CMC's.

## FEATURES OF SILICA INFLUENCE ON PYROLYTIC PROCESSES OF HYDRATED CELLULOSE WHILE OBTAINING SILICON CARBIDE FIBERS.

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Keywords: fibers, SiC-fibers, synthesis, hydrated cellulose

The present paper is devoted to physico-chemical transformation of hydrated cellulose impregnated by silicate of alkaline metal solutions while obtaining of SiC-fibers by method of carbothermal reduction. Hydrated cellulose fibers together with silica additions were subjected to heat treatment at temperatures up to 2000 °C in various media (Ar, N<sub>2</sub>, air). The methods applied were chemical analysis, X-ray diffractometry, derivatography, IR-spectroscopy, electronic and scanning microscopy.

It was found that the presence of silica in the hydrated cellulose fiber composition essentially affects the pyrolysis processes of hydrated cellulose. The results of gravimetric, dilatometric and difference-thermal analysis show that dehydration processes of hydrated cellulose containing SiO<sub>2</sub> additions accompanied by shrinkage occur in the much lower temperature area (~for 50 °C) comparing to pure hydrated cellulose. The presence of silica also decelerates shrinkage and reduces its magnitude in 2-2,5 times depending on its quantity containing in hydrated cellulose. The carbon yield as the result of carbonization is three times as much in the presence of silica which can be explained by inhibition of reaction forming L-glucosan. The results of X-ray diffractometric analysis confirm that silica has a structure-forming influence upon the carbonizate and graphite (002) peaks appear on X-ray photographs of samples treated at 750-850 °C. As it was found the reaction of SiC forming begins at the temperatures about 1000 °C.

The results obtained allow to optimize the technology of receiving SiC fibers from hydrated cellulose by carbothermal reducing method.

## **Fine Silicon Carbide Fiber Synthesized from a Silicon-based Polymer Blend Using Radiation Curing**

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**Keywords:** SiC fiber, Polycarbosilane, Polyvinylsilane, Polymer blend, Radiation curing, CMC

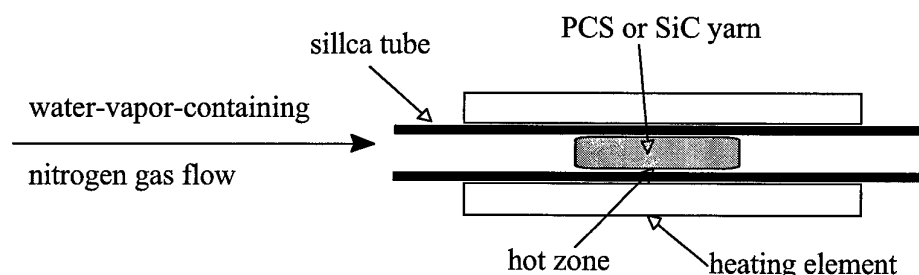
At present in the industry, Silicon carbide (SiC) fiber, which is one of the likeliest candidates as a reinforcement fiber of ceramic matrix composites (CMCs), is synthesized from polycarbosilane (PCS) through melt-spinning, curing, and pyrolysis processes. The diameter of thus commercially available SiC fibers is 10-15 $\mu$ m. In order to fabricate CMCs with 3-dimensional complex shapes, it is important to develop a SiC fiber with diameter of less than 10 $\mu$ m, flexibility, and high strength. We have examined the method of melt-spinning of fine polymer fiber as an approach to obtain finer SiC fiber. However, it is difficult to obtain fine polymer fiber from PCS because the spinnability of PCS is not so good. In order to improve the spinnability of precursor polymer, we have blended polyvinylsilane (PVS), which is a viscous liquid polymer at room temperature, to PCS as a spinning additive. According to relationship between temperature and melt viscosity of the polymer blend, it was found that the precursor polymer can be melt-spun at temperature (about 490K), 110K lower than PCS (about 600K), and that the spinnability of the precursor polymer is improved by blending PVS. Fine polymer fiber was obtained from the polymer blend, and it was cured by electron beam irradiation and then pyrolyzed. Finally, very fine and flexible SiC fiber that has the average diameter of 6 $\mu$ m was synthesized from the PCS-PVS polymer blend. Such fine SiC fiber is woven into various types of fabrics, and these are expected as the reinforcements of CMCs with complex shapes.

## Influence of water-vapor-containing atmosphere on the pyrolysis of polymer-derived SiC fibers

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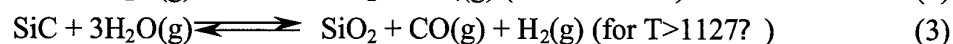
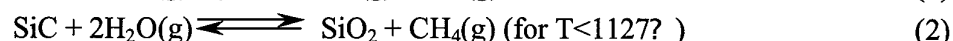
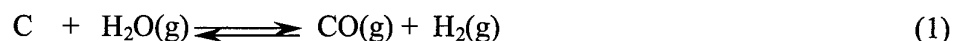
**Keywords:** SiC fiber, polymer-derived, mechanical property, firing, water vapor

The development of the Nicalon fibers, obtained by pyrolysis from organic or organometallic polymeric precursors, is exciting considerable interest as it offers the possibility of developing a new generation of composites for high temperatures. The precursor route has some important advantages with respect to more conventional techniques: (1) it requires lower temperatures, (2) polymeric precursors can be obtained under different states before firing (e.g. as bulk bodies, green films or fibers), (3) polymeric precursors are available with a variety of compositions as single species or as mixtures, a feature allowing the design of ceramics with specific properties. However, the pyrolysis processing also has some inner disadvantages. Weight loss caused by the evolution of small species such as hydrogen and methane is fatal to the mechanical properties of SiC fibers, because many defects are formed during the pyrolysis process. The theoretical tensile strength of SiC fibers is about 70GPa, whereas the real tensile strength of so-obtained SiC fibers is just 2GPa to 3GPa. Factors that influencing the mechanical properties of SiC fibers is complicated from the polymer structure to the firing atmosphere. This paper focused on the water-vapor-containing firing atmosphere on the ultimate mechanical properties of SiC fibers.



Schematic diagram of the set up used in the study

Different content of water vapor was mixed to the high-purity nitrogen gas, which demonstrates different qualities of high-purity nitrogen. Results revealed that the water vapor remarkably reduced the tensile strength. The reaction mechanism was analyzed through IR, AES, XPS and SEM.



Pitting defect was frequently occurred on the water-vapor-etched SiC fibers, which was covered with a slight SiO<sub>2</sub> film.

## **A novel Si-N-C fiber with a low oxygen content prepared from a vinyl-containing polysilazane precursor (I) polymer synthesis**

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**Keywords:** Si-N-C fiber, cyclo-methylvinylsilazane, vinyl, polysilazane, synthesis

The first-generation polymer-derived ceramic fibers, such as Nicalon (Si-C-O) and MPDZ (Si-C-N-O), are fabricated from air-cured polycarbosilane or polysilazane fibers. Whereas, a much content of oxygen (10-15wt%) restricts their applications not greater than 1200°. To increase their thermostabilities at elevated temperatures, therefore, the second-generation ceramic fibers with little oxygen content were prepared (from radiation-cured precursors, for example). Hi-Nicalon (Si-C) and HPZ (Si-N-C) are their representatives. But it also has a question of high absorbed dose, 10~15MGy for Hi-Nicalon and 2-4MGy for Si-N-C, that makes it hard on irradiation equipment and low in efficiency.

In an attempt to reduce irradiation dose and make cheap oxygen-free ceramic fibres, we have prepared a kind of vinyl-containing precursor by introducing cyclo-methylvinylsilazane (CMVSZ) to the polycarbosilanes (PCSs) or polysilazanes (PSZs). Thus, low-oxygen-content SiC and Si-N-C fibers were successfully obtained at lower absorbed doses. The Si-C fiber has been released previously, and this paper, with two parts, is to make a thorough study on the fabrication and characterization of the Si-N-C fiber.

The vinyl-containing polysilazane (VPSZ) was prepared as following. First,  $\text{ViMeSiCl}_2$  was mixed with benzene in a three-necked flask with a reflux condenser and a thermometer. After the air in the flask had been replaced with dry  $\text{N}_2$  gas,  $\text{NH}_3$  was introduced into the system accompanied by high-speed stirring. The reaction mixture was filtered and distilled and the resultant, cyclo-methylvinylsilazane (CMVSZ), was ready for the third step. Second,  $\text{Me}_2\text{SiCl}_2$  and  $\text{MeHSiCl}_2$  with a ratio of 1.5:1 were similarly co-ammonolyzed. The product was then put into a reaction vessel with a quartz reactor tube and heated slowly in  $\text{N}_2$  gas flow up to 350°C. A PSZ with a melting point of 120~128°C was obtained after cooling. Then, the CMVSZ with a specific mass percent (5-20wt%) was added to the above vessel. After thermal copolymerization was carried out at 260°C for 30 min, the VPSZ precursor with a various vinyl content (0.0-4.50wt%) was synthesized.

The spinnability of the VPSZ polymer is also discussed in PART I, which shows a little decrease of spinnability with little CMVSZ added and, if much CMVSZ added, the VPSZ will be nearly unspinnable. Finally, VPSZ green fiber with a various vinyl content was prepared.

## **Novel Ceramic SiCN-Fibers Derived from the Polycarbosilazane ABSE**

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**Keywords:** SiCN-fibers, polycarbosilazane, meltspinning, electron beam curing, pyrolysis

In the last twenty years the development of fiber reinforced ceramic matrix composites as constructing materials for high temperature applications is an important field of materials research. These CMCs have to fulfill many engineering requirements like improved chemical and mechanical high temperature properties combined with low-cost processing.

For the required high temperature properties of the CMCs ceramic fibers with high strength, sufficient thermal stability, high oxidation and creep resistance, low density and sufficient weavability are necessary. One of the main problems for manufacturers of CMCs is that low-cost ceramic fibers with sufficient high temperature properties are commercially not available. Whereas high temperature stable fibers are too expensive for extended industrial applications, low-cost fibers are limited by their operating temperature.

The aim of this work was to develop a low-cost ceramic fiber with required mechanical properties up to 1400 °C under oxidizing atmosphere. For fiber spinning the self-synthesized polycarbosilazane ABSE was used, which is a low-cost precursor if it is produced on an industrial scale. Polymer fibers with diameters between 10 and 30 µm were produced by a meltspinning process and subsequently cured by electron beam with different irradiation doses under inert conditions. The as-spun and the cured fibers were characterized by thermogravimetric analysis (TGA), FTIR- and MAS-NMR-spectroscopy, scanning electron microscopy (SEM) and energy-dispersive analysis of X-rays (EDA). Pyrolysis up to 1400 °C was performed in a nitrogen flow using graphite and alumina furnace environments. The ceramic fibers were investigated by elemental analysis (EA), TGA, FTIR- and MAS-NMR-spectroscopy, SEM, EDA and X-ray diffraction (XRD). For selected fiber samples mechanical properties were determined. The oxidation behavior of these new SiCN-fibers was examined by heat treatment in air at different temperatures up to 1500 °C and characterized by SEM.



## **Preparation of non-oxide ceramic fibers in the system Si-C-N and Si-B-C-N**

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Keywords: precursor, ceramic fibers, rheology, chromatography, fiber spinning

Si-C-N and Si-B-C-N based ceramics are very interesting materials for high temperature applications due to their amorphous structure which is retained up to relatively high temperatures. This structure leads to good mechanical properties and a good creep resistance up to temperatures of 1500°C and 1800°C for Si-C-N and Si-B-C-N, respectively. To achieve homogeneity of the material on the molecular level, preceramic precursors are used to synthesize these materials.

In order to get information about the processability of these precursors, examinations of the molecular structure and the rheological behavior have been conducted at our institute using well-known tools of macromolecular chemistry as gel permeation chromatography (GPC) and rheometry.

Goal of the research is to modify the precursor systems in a way that they have optimal processing properties for a given application. This can either be done by adjusting the synthesis conditions in order to get the proper molecular structure or by using additives which are blended with the precursors to achieve adequate rheology. In any case the relation between molecular structure and flow behavior needs to be analyzed, if this optimization shall be done.

Our main interest is the optimization of precursors for fiber spinning. We have studied a solvent based Si-B-C-N precursor as well as a meltable Si-C-N precursor which initially showed both Newtonian flow behavior and therefore did not show good spinnability. It could be clearly shown by gel permeation chromatography that the low molecular weight (between 1000 and 2000 g/mol) obtained by the synthesis is the reason for the observed rheology.

In the case of the Si-B-C-N precursor Poly(4-vinylpyridine) has been added in such a quantity that optimal fiber spinning behavior was obtained. Poly(4-vinylpyridine) (in pyridine as solvent) was the only organic polymer which fulfilled all requirements of an spinning additive which are compatibility with the precursor without phase separation, achievement of the proper rheology without gelling, and complete decomposition during pyrolysis.

In the case of the Si-C-N precursor which is also of low molecular weight after synthesis, a modification step can be conducted in order to get meltable precursors with proper spinning rheology. GPC measurements help to optimize the thermal treatment which induces the condensation. The GPC data show that polymeric chains with molecular weights up to  $10^6$  g/mol are formed which leads to pronounced viscoelasticity and very good spinnability. An addition of organic polymers is not necessary in this case.

With both precursor systems fibers have been produced on the lab scale. The green fibers have been crosslinked either by treatment with ammonia or by electron irradiation. The crosslinked fibers have been pyrolyzed in inert atmosphere to obtain amorphous ceramic fibers. Si-C-N ceramic fibers show good stability in oxidative environment.

## New Fiber Precursors in the System Si-B-N-C

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Keywords: new precursors, fiber processing, fiber properties

In the last years, the system Si-B-N-C was proven to be a promising candidate for chemically resistant and high-temperature stable materials, especially fibers. From the precursor molecule TADB (trichlorosilylamino-dichloroborane), a polyborosilazane is obtained via aminolysis and thermal polycondensation. This polyborosilazane can be thermally treated to form X-ray amorphous ceramic fibers that show good mechanical properties as well as an extraordinary stability against high temperatures – even in oxidizing atmospheres.

In the recent years, problems have been caused preliminarily by difficulties in reproducing the rheological properties of the polyborosilazane obtained from TADB, which in turn have caused difficulties in the fiber-spinning process. By modifying the substituents at Si and/or B, polyborosilazanes with “tailored”, well reproducible rheological properties were obtained. Furthermore, a new polycondensation process leads to an improved homogeneity of the polymers.

Besides of the rheological properties and spinnability of the polymers, the curing of the green fibers was an important topic of our research. A combination of suitable substituents at Si and/or B with a suitable curing gas offers the possibility to achieve a rather fast ( $< 3$  s) fiber curing.

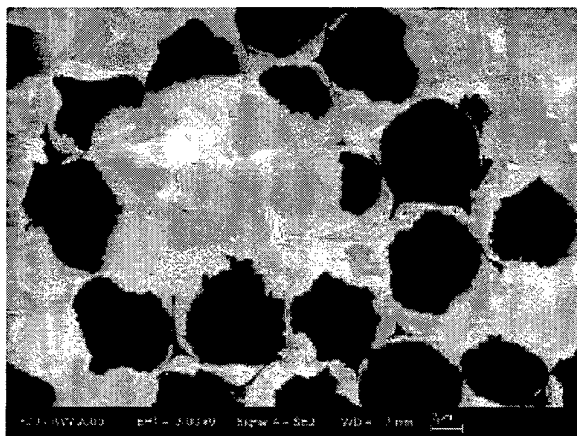
First results on pyrolyzed and sintered fibers reveal a wide potential for future applications.

## Origin and Effect of Fiber Attack for the Processing of C/SiC

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**Keywords:** carbon fiber, silicon carbide, LSI-process, silicon monoxide

Among the several different processing routes for carbon fibre reinforced silicon carbide (C/SiC), the liquid silicon infiltration (LSI) process of porous carbon preforms is one of the fastest and most cost-effective. The time consuming gas phase infiltration of the CVI-process and the repeated impregnation and pyrolysis steps of the liquid polymer infiltration (LPI) route can be avoided. Furthermore, the raw materials phenolic resin and silicon powder are inexpensive in comparison to the silicon-organic polymers used in the LPI process. On the other side, mechanical properties of LSI-made materials stand behind those of the competing processes. This is due to the high reactivity of the silicon melt against carbon, which results in severe attack of the carbon fibers. As one can see from the figure below, the fibers are closely embedded and interconnected with the SiC matrix. Therefore, essentially



2D-C/SiC with massive carbon fiber attack after liquid silicon infiltration for 1h at 1450°C

they lost their capability of toughening the brittle ceramic matrix.

The focus of the present work aims at the understanding of the mechanisms which take place during, and may be before, the silicon melt infiltrates the porous body and reacts with the available carbon. Typical processing conditions are vacuum and temperatures between 1450-1600°C. As the technical silicon powder always contains oxygen up to 2wt.%, the formation of SiO has to be taken into consideration. This species is known to react with carbon under formation of porous and fine-grained SiC-crystals. In our investigations we found that similar morphologies are always present in vicinity of the residual carbon, both fiber and matrix associated.

From the literature it gets visible that several research efforts exist to protect the carbon fibers from the aggressive silicon melt. This can be done by coatings from Pyro-C, SiC or BN. For these developments it might be of interest what kind of gas reactions also may influence the microstructure of C/SiC composites fabricated by the LSI-route.

## Thermally-induced degradation of Nextel™ 610, 650, and 720 fibers - a microstructural study

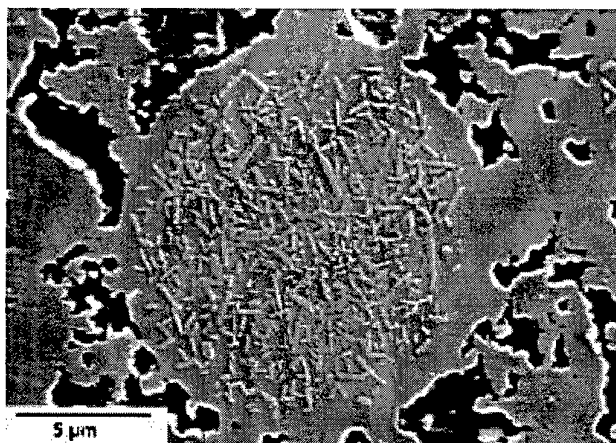
M. Schmücker, F. Flucht, B. Kanka, H. Schneider, Deutsches Zentrum für Luft- und Raumfahrt e.V. ,  
Institut für Werkstoff-Forschung , Köln, Germany

**Keywords:** oxide fibers, characterizatzion, Whipox CMC

Superior strength is required for oxide fibers when applied for the reinforcement of ceramic bodies. Commercial alumina-based fibers of the Nextel™ (3M) family show decent strength values (2-3 MPa) as a result of sub-micron grain size. The fine-grained microstructure, however, is not stable from thermodynamical point of view, and hence coarsening at elevated temperatures has to be expected. Since the activation energy of diffusional processes is relatively low in oxides in comparison with non-oxide ceramics, microstructural changes will occur above about 1000 to 1200 °C.

In the present study microstructural changes and related strength degradation of Nextel 610 (virtually pure alumina), Nextel 650 (alumina plus zirconia), and Nextel 720 fibers (alumina plus mullite) are investigated in the temperature range of 1200 to 1600 °C. Though microstructural coarsening can be detected in all fibers after firing above 1200 °C (1h) it becomes obvious that Nextel 610 and Nextel 650 fibers are much more affected by heat-treatment than Nextel 720.

The studies on the thermally-induced degradation of alumina based fibers have been completed by investigations on their high-temperature stability in WHIPOX™ all oxide composites. In Whipox oxide/oxide composites uncoated oxide fibers are embedded in a highly porous mullite-type matrix being slightly supersaturated in SiO<sub>2</sub>. Above 1500 °C fiber/matrix interactions do occur: In case of Nextel 610 and Nextel 720 fibers mullite forms at the fiber rims as a result of a reaction between Al<sub>2</sub>O<sub>3</sub> of the fiber and free silica of the matrix. Degradation of uncoated Nextel 650 fibers within the porous mullite matrix is even stronger. Above 1500 °C the fibers are virtually destroyed and increasing densification of the porous matrix occurs due to enhanced sintering.



Whipox CMC heat-treated at 1600 °C: The Nextel 720 fiber shows grain coarsening and a depletion of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in the rim area.

## Influence of High Temperature Argon Heat Treatment on Tensile and Thermal Properties for Four Types of BN/SiC Coated SiC Fiber Preforms

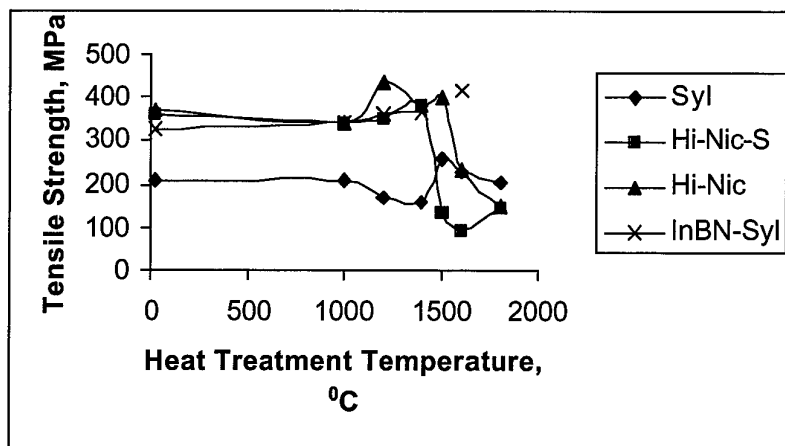
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**Keywords:** SiC fiber preforms, Tensile strength, Thermal conductivity.

Boron nitride (BN)/ silicon carbide (SiC) coated SiC fiber preforms are being used as starting material for fabrication of SiC fiber-reinforced silicon carbide matrix composites by the melt infiltration approach. These composites invariably contain up to 15 wt% of residual silicon that limits upper temperature capability of the composites to 1200°C. To develop SiC fiber reinforced ceramic matrix composite system stable to 1400°C, the current SiC/Si matrix must be replaced with a more refractory matrix requiring processing temperatures up to 1650°C.

The current study was performed to determine strength and dimensional stability of SiC fiber preforms under high temperature processing conditions,. In this study, room temperature physical, tensile, and thermal properties of four types of BN/SiC coated SiC fiber preforms, Hi-Nicalon®, Hi-Nicalon-S®, Sylaramic®, and insitu-BN Sylaramic®, were measured before and after heat treatment in 0.1 MPa argon atmosphere at temperatures to 1800°C for 1 and 100 hrs. Preliminary results indicate that the Sylaramic®, and Insitu-BN Sylaramic® preforms retain their as produced strengths after 100hr exposure, but the Hi-Nicalon®, and Hi-Nicalon-S® preforms show strength degradation after 1h exposure beyond 1500°C. The mechanism of strength degradation for the two types of Hi-Nicalon® preforms, and the influence of heat treatment on transverse thermal conductivity for these preforms will be discussed.

Influence of 1h argon heat treatment on room temperature tensile strength for BN/SiC coated SiC fiber preforms



## **Microstructural evolution and mechanical behaviour up to 1500°C of Nextel 720 mullite-alumina fibres**

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keywords: fibre, Nextel 720, mullite, alpha alumina, high temperature behaviour, creep, exsolution, abnormal grain growth

The microstructure and tensile properties of the as-received and heat-treated Nextel 720 fibre have been studied. During its fabrication the Nextel 720 fibre is pyrolysed at a temperature lower than 1400°C for a very short time which does not allow the microstructure to be stabilised. A pseudo-tetragonal metastable, alumina rich, mullite is formed which crystallises in the form of mosaic grains containing low angle boundaries. These mosaic grains enclose some rounded and elongated  $\alpha$ -alumina grains.

The effects of heat treatments in air on the fibre microstructure and room temperature mechanical properties will be first described. The evolution of the mullite to the stable orthorhombic symmetry is seen from 1200°C for post heat treatments lasting several hours. For longer heat treatments at 1200°C or at 1300°C and higher temperatures, the mosaic grains begin to recrystallise into single grains. Alumina, rejected from the mullite, contributes to the growth of elongated  $\alpha$ -alumina grains which suggests diffusion through an intergranular liquid silicate phase. At 1400°C the mullite has the equilibrium 3:2 composition and after 24 hours the growth of the elongated  $\alpha$ -alumina grains leads to a reduction of the room temperature tensile strengths. The increase in  $\alpha$ -alumina content, coupled with the phase transformation and dissolution of mullite leads to an increase of the Young's modulus after heat treatments from 1200°C.

The behaviour of the fibre under load at high temperature will be then presented. Creep experiments have been conducted up to 1500°C. The Nextel 720 fibre shows the highest resistance to creep when compared to all other commercial fine oxide fibres. The creep mechanisms involve the dissolution of mullite and reprecipitation of alumina into elongated grains as well as grain boundary sliding through a silicate intergranular phase. The fibre is however very sensitive to alkaline contamination inducing, under load from 1200°C, an abnormal alpha-alumina grain growth reducing dramatically its tensile strength and time to failure in creep.

## **Failure Analysis of NEXTEL™ 720 Fibers Subjected To High-Temperature Testing in Air**

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**Key words:** NEXTEL™ 720 fiber, fiber impurities, time-dependent failure, fractography

NEXTEL™ 720 fibers (3M, St. Paul, MN/USA) are prone to time-dependent failure (SCG) at  $T \approx 1000^\circ\text{C}$  and show loss of structural integrity upon annealing at  $T \geq 1200^\circ\text{C}$  in air. Although different impurity sources have been reported in the literature, the true mechanism of generating critical failure-related defects during high-temperature testing of NEXTEL™ 720 fibers has not yet been unequivocally addressed.

Previous research conducted in our laboratory has shown that that room temperature strength as well as the SCG characteristics are left unaffected by intrinsic fiber impurities. The corresponding fracture origins did not correlate with impurity segregation effects. However, fracture surfaces of NEXTEL™ 720 fibers tested at  $T \geq 1200^\circ\text{C}$  were entirely covered by newly formed lath-shaped crystalline phases which frequently exhibited high calcium concentrations.

We present a fractographic analysis of NEXTEL™ 720 fibers tested in the critical temperature range in excess of  $1200^\circ\text{C}$ . The actual fiber degradation process which eventually results in the formation of a Ca-rich impurity sink is monitored through the combined approach of optical microscopy, SEM and TEM investigations. Strategies are offered to improve the service temperature of NEXTEL™ 720 fibers for high-temperature applications.

## Microstructural Response Of $\text{SiBN}_3\text{C}$ -Fibers Upon Annealing In Oxidizing And Reducing Atmospheres

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**Keywords:**  $\text{SiBN}_3\text{C}$ -fibers, annealing, microstructural development, transmission electron microscopy

In recent years novel ceramic fibers of nominal  $\text{SiBN}_3\text{C}$  composition have been synthesized via pyrolysis of a preceramic polyborosilazane employing a „single source“  $\text{Cl}_3\text{Si-NH-BCl}_2$  (TADB) precursor. Despite their amorphous nature in the as-processed condition these fibers have demonstrated excellent high-temperature stability and are less prone to time-dependent failure as compared to conventional SiC-based fibers.

On a nanometer scale, the  $\text{SiBN}_3\text{C}$  fiber exhibits characteristic microstructural changes upon annealing in oxidizing and reducing atmospheres respectively which have been studied by means of high-resolution and analytical transmission electron microscopy (HREM, AEM). Even short-term annealing at  $1500^\circ\text{C}$  in air introduces a well pronounced double-layer structure enveloping an isotropic  $\text{SiBN}_3\text{C}$  fiber core left unaffected by oxidation, that is, a (i) two-phase „bottom surface layer“ consisting of an amorphous Si-B-N-C matrix along with turbostratic h-BN particles followed by a (ii) single-phase amorphous silica „top surface layer“. Upon annealing in a reducing (nitrogen) atmosphere the formation of a two-phase „SiC plus h-BN“ surface layer is observed while HREM of the former amorphous fiber core provides evidence for local partial crystallization.

The formation mechanisms of the different surface layers are discussed including the effect of impurities during annealing of the  $\text{SiBN}_3\text{C}$  fiber.

This research has been funded by BMBF under grant 03N3038A1 („Langzeitbeständige, faserverstärkte Keramiken für die Verkehrs- und Energietechnik“). Approval of publication by the Bayer AG is gratefully acknowledged.



## Characterization of Oxidized Si(B)C(N) Fibers

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Keywords: characterization, fibres, oxidation, strength

The oxidation resistance of nonoxide fibers is important in determining their suitability for use in ceramic-matrix composites for applications in high temperature, oxidizing environments. The oxidation behavior of one commercially available fiber and two developmental amorphous fibers was investigated. The commercially available fiber was Ube's Tyranno SA, which is a polycrystalline  $\alpha$ -SiC fiber. One exploratory fiber was the Bayer-Fraunhofer SiBCN fiber, which is fully amorphous as received, while the second was a fully amorphous SiCN fiber obtained from the University of Bayreuth. Fibers were heat treated in stagnant laboratory air at temperatures of 1300°–1500°C for 1 or 2 h.

At 1500°C, oxidation of the SiC fiber produced a single surface layer of cristobalite, while the other fibers contained two or more distinct oxidation layers at the surface. The SiCN fiber contained two layers of oxide product. An inner layer of amorphous silica and an outer layer of cristobalite. The oxidized SiBCN fiber contained three distinct concentric oxidized layers, each increasing in oxygen concentration from the core to the outer surface. The unreacted fiber core retained its amorphous nature. The first oxidation layer next to the core consisted of a mixture of amorphous SiBCNO and turbostratic BN, which evolved into a more oxygen-rich glass with hexagonal and turbostratic BN grains dispersed throughout nearer the surface. The second layer consisted of essentially pure silica glass with no detectable B, C, or N present. The thin outermost layer was cristobalite. At lower oxidation temperatures the outer silica layer remained amorphous. All fibers exhibited significant strength degradation after oxidation. Oxidation kinetics were determined and compared with data available in the literature for other SiC-based fibers and pure SiC and Si<sub>3</sub>N<sub>4</sub>.

## High-Temperature Oxidation of Non-Oxide Ceramic Matrix Composites

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Keywords: SiC-fibers, high temperature oxidation, oxygen diffusion, oxidation protection

In recent years there has been much progress in the development of nonoxide ceramic fibers (SiBN(C), SiC) that have a high temperature and oxidation resistance.

The oxidation behavior of these fibers was found to be comparable with the of pure monolithic materials, e.g. HIP-Si<sub>3</sub>N<sub>4</sub> or CVD-SiC. These results could be obtained as the consequence of the formation of a oxidation surface layer of pure silica. The minimal coefficient of oxygen diffusion of this silica layer was found to be the reason of the superior oxidation stability of these materials. The long-term oxidation of these materials obeyed a parabolic mechanism with the formation of the silica surface layer of less than 0.1 mm<sup>2</sup>/h.

As a example of the high oxidation stability of such ceramic fibers SiC fibers (UBE SA3) were oxidized at 1500°C, 200 h. After this oxidation treatment the formation of a surface layer of silica of about 2 µm was observed. However, in spite of the excellent oxidation resistance of the fiber already a third of the effective cross section (about 10 µm) has been consumed after only 200 h oxidation in air.

For that reason effective oxidation protection methods are required in order to fabricate long-term high-temperature CMC's.

In the present study the oxidation behavior of SiC-fiber based composites (UBE SA3) with a Si<sub>3</sub>N<sub>4</sub>-MoSi<sub>2</sub> matrix has been studied. The composites have been produced by infiltration of ceramic fiber bundles with various slurries, winding by a computer controlled winding-up module and the thermal treatment. The microstructure of the resulting CMC was characterized before and after oxidation treatment. As the consequence of a modified oxidation mechanism of the matrix the ceramic fibers were found to be protected from the oxygen attack resulting in an improved oxidation resistance of the composite.

## Standardization of Test Procedures for the Tensile Evaluation of Ceramic Fibers

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In 1997 the jurisdiction of the former ASTM Standard Test Method D3379 "Standard Test Method for Tensile Strength and Young's Modulus for High-Modulus Single-Filament Materials" was transferred from ASTM committee D30 on *High Modulus Fibers and Their Composites*, to committee C28 on *Advanced Ceramics*. One year later this document was withdrawn, in part because it was demonstrated that the recommendation of using the average of the cross-sectional area of a collection of fibers for the calculation of individual fiber strengths was inappropriate. Lara-Curzio and Russ [1] showed with Monte Carlo simulations that significant errors were incurred in the determination of individual fiber strengths, and on estimates of the parameters of the distribution of fiber strengths, when fiber strengths were determined using the average cross-sectional area of a collection of fibers.

Recently it has been shown that the diameter of most ceramic fibers is not constant, but that it varies along the length of each fiber [2-5]. Using Monte Carlo simulations Lara-Curzio and Garcia [6] have provided estimates of the magnitude of the error that is incurred in the determination of each fiber strength and on estimates of the parameters of the distribution of fiber strengths, when the strength is calculated using a value of the fiber cross-sectional area that doesn't correspond to the fracture plane.

This poster presentation will describe the draft of a standardized test method for the tensile evaluation of single fibers that is currently undergoing through the ASTM balloting process and that incorporates provisions for addressing the issues outlined above.

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**KEYWORDS:** fiber, strength, standard test method, Weibull, diameter, ASTM, tensile

This work was sponsored by the US Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

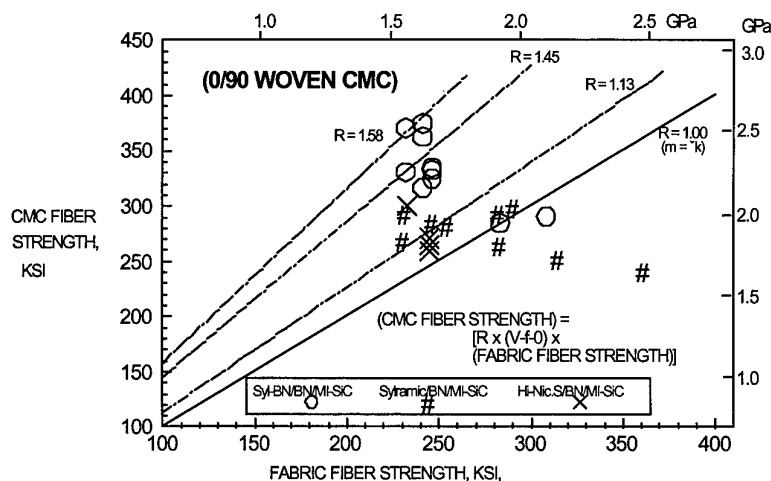
## Effects of 2-D Fabric Geometry on the Tensile Strength of Stoichiometric SiC Fiber-Reinforced Composites

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NASA Glenn Research Center  
Cleveland, Ohio 44135, U.S.A.

**Keywords:** SiC fiber, SiC fabric, thermal treatment, architecture, SiC/SiC composites, tensile fracture

Near stoichiometric SiC fibers demonstrate superior thermo-mechanical properties that are essential for high-temperature structural CMC. Hi-Nicalon Type S from Nippon Carbon, Sylramic from Dow Corning and Composites Optics, and treated Sylramic-BN from NASA are leading candidates. The NASA-treated Sylramic-BN even further improves the creep resistance and surface composition of Sylramic fibers. Currently, most SiC/SiC CMC are fabricated with 2-dimensional 0/90 degree woven fabric, and it is believed that a successfully woven fabric is a most important step for a successful CMC. That is, high fabric strength typically results in high CMC tensile strength if the CMC fabrication processes do not degrade fiber strength. NASA has made tensile fracture strength measurements on tows of various fiber types at room temperature, both for as-received and coated fibers, and found for the near-stoichiometric SiC fibers with rough surfaces that the sizing and coating significantly affected the fracture characteristics by minimizing or altering fiber-to-fiber mechanical interactions. In 2-D fabric, each tow is much tighter than a single individual tow, which typically results in lower tow strengths for the woven fabric. Several approaches appear to exist to reduce fiber-to-fiber contact: lower tow-ends per inch (epi), lower crimp angle from cross-over tows, improved methods for fiber separation, and treatments to in-situ form a compliant layer on the fiber surface. Indeed, it has been observed that CMC using treated Sylramic-BN fiber with low epi showed a high modulus followed by a graceful cracking at a high proportional limit, and high ultimate strength and strain, up to 0.5GPa and 0.5 %. This tensile behavior is analyzed in terms of fabric geometry and compared with those of CMC reinforced by un-treated Sylramic and Hi Nicalon S fibers with a higher epi.

EMP. RELATIONSHIP BETWEEN PRE-PREGGED FABRICS  
AND MAX. CMC TENSILE STRENGTHS AT R.T.

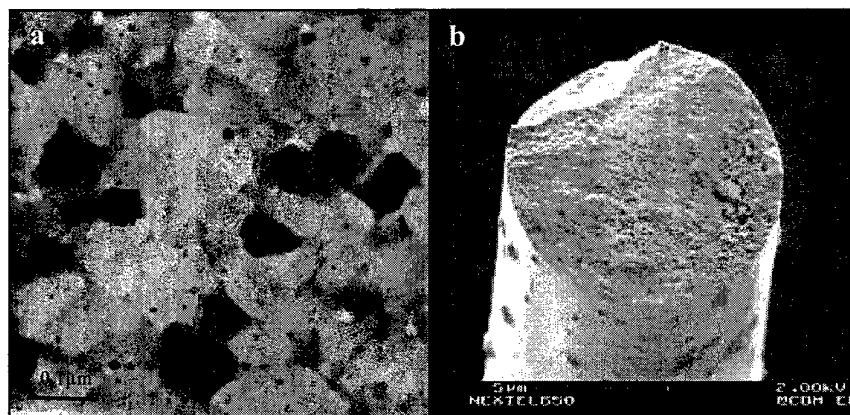


## Mechanical and Microstructural Characterisation of the Nextel 650 alumina zirconia fibre

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**Keywords :** Nextel 650, alumina-zirconia fibres, properties, creep, microstructure

Oxide fibres have an obvious chemical advantage over non-oxide fibres for use at very high temperatures in oxidising or corrosive environments. Many polycrystalline oxide fibres have been developed both for refractory insulation and as structural reinforcements. These fibres are often based on alumina. However they have usually been found to suffer from loss of mechanical strength from around 1000°C. Creep behaviour of polycrystalline alumina can be improved by the inclusion of zirconia particles which act to pin the structure and modify intergranular diffusion. This was clearly shown by the comparison of the creep behaviours of the PRD-166 fibre containing 20wt% of yttria stabilised tetragonal zirconia and the pure alumina Fiber FP both produced by Du Pont. 3M has produced both a pure  $\alpha$ -alumina fibre, the Nextel 610, and a one consisting of  $\alpha$ -alumina containing 10wt% of yttria stabilised cubic zirconia fibre, the Nextel 650 fibre. These fibres have smaller diameters than the Du Pont fibres as well as higher strengths, due to finer grain structures. Publications from 3M indicate that the Nextel 610 fibre creeps at a higher rate than the FP Fiber but that the Nextel 650 creeps at a lower rate than the PRD-166 despite the finer grain size.



Microstructure (TEM) and fracture surface (SEM) of the Nextel 650 fibre

This paper will discuss the mechanisms controlling strength and creep in the Nextel 650 fibre by a parallel study of the microstructure and mechanical properties and by a comparison with the three other fibres mentioned above. The microstructure of the Nextel 650 is shown in Figure 1a and is composed of alumina grains of 100 nm in size together with zirconia grains which present a bi-modal grain size distribution as zirconia grains of 5-10 nm are found within the alumina grains and 20-30nm grains can be found at triple points. Figure 1b shows the failure morphology of the fibre. Very little scatter in diameter has been observing indicating a close control over the manufacturing process. The single filament room temperature strength of the Nextel 650 fibres has been determined to be  $2.3 \pm 0.3$  GPa, which is 20% less than that of the Nextel 610 fibres with less of a length dependence of strength than seen with the other fibres considered. The evolution of the failure strength as a function of temperature has been studied and with certain strain rates super plastic behaviour has been observed at 1200°C. The effect of strain rate on strength at high temperatures will be reported as will the effects of heat treatments. The thresholds for creep as a function of temperature and applied stress will be revealed and the mechanisms governing these behaviours will explained in terms of the fibre microstructure as observed by SEM and TEM.

## Creep Behaviour of Single SiNO – Fibres

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Universität Bremen, Germany

Keywords: creep, SiNO, single fibres, oxidation

The high temperature behaviour of prototype SiNO fibres is studied in terms of creep and oxidation behaviour. The amorphous fibres are processed applying a high temperature CVD process established by EMPA (Swiss Federal Laboratories for Material Testing and Research). Single fibres reach a length of about 50 mm while diameters vary between 1 and 60  $\mu\text{m}$ . The samples often show different features, such as bends, junctions, zigzags, curls or a vermicular appearance. Straight fibres with smooth surfaces are also found; these isolated fibres are investigated in this study.

A new setup, particularly designed for testing short fibres, was applied to carry out creep tests at temperatures between 1200°C and 1450°C. The fibres are fixed in warm grips outside a micro furnace with a heating zone of only 10 mm. Mechanical load is applied using an adjustable dead weight system. Thus, the stress can be set depending on the fibres diameter. The elongation of the fibre was measured via a contactless capacitive gauge length method. In order to investigate the oxidation behaviour fibres were annealed in air and argon. Scanning electron microscopy (SEM), energy dispersive x-ray analysis (EDX) and x-ray diffraction (XRD) were applied to monitor structural changes after testing.

No creep strain occurs at testing temperatures lower than 1300°C. Creep rates were found to be stationary and very small at temperatures below 1400°C. At higher temperatures also tertiary creep was observed and fibres finally failed after up to 380 h at nominal stresses between 100 MPa and 500 MPa. In air the creep behaviour is strongly reduced by pretreatment under creep conditions at lower temperatures. Thermal gravimetric analysis under oxidizing conditions displays a significant weight gain at temperatures above 1120°C. SEM images and EDX analysis of annealed and creep tested fibres show an amorphous passivating oxide layer on the samples which consists of crystalline  $\text{SiO}_2$  after annealing 12h in air at  $T \geq 1400^\circ\text{C}$ . It can be followed that the creep strain is mainly attributed to oxidation process leading to a reduction of the load bearing cross section of the fibre. Furthermore a weight loss of about 28% is observed at fibres that are annealed 12 h in argon at  $T \geq 1400^\circ\text{C}$ . At these temperatures the fibres degrade giving rise to high creep rates and failure.

## Microscopic thermal characterization of C/C-SiC

Jumel J.<sup>(1,2)</sup>, Lepoutre F.<sup>(1)</sup>, Roger J.P.<sup>(2)</sup>, Friess M.<sup>(3)</sup>, Krenkel W.<sup>(3)</sup>, Neuer G.<sup>(4)</sup>.

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**Keywords:** C/C-SiC composites, thermal characterization, microscopy, photorefectance

The C/C-SiC composites /1/ have complex microstructures in which the components (matrix and fibers, see figure 1) are often not characterized precisely. Such a lack of knowledge has important consequences, for instance it makes difficult the use of theoretical simulations in which it is essential to supply the numerical codes with the correct microscopic physical properties /2/. At the size of these components, conventional methods are generally unpractical and the modulated photothermal methods /3/ which operate without any contact at scales ranging from micrometers to millimeters have demonstrated their interest. Among them, the photorefectance microscopy /4/ has a large enough spatial resolution to characterize the thermal properties in a 8 micrometers carbon fiber (figure 2).

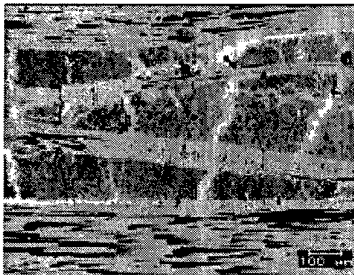


Figure 1: Microstructure of a C/C-SiC composite showing the various elements (matrix and fiber) to characterize

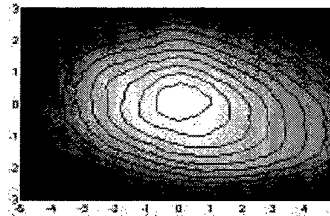


Figure 2: Amplitude of the periodic temperature field (10µm x 6µm) generated in a carbon fiber around an heating point. The anisotropic heat diffusion is materialized by the quasi-elliptic isotherms observed.

In a first step, we present the principle of this technique and the thermal parameters extraction scheme used to interpret the measurement in the different phases of the matrix of a C/C-SiC composite, and in several carbon fibers. Our results are correlated to the morphology of the material and enable to quantify the effect of the process parameters on the microscopic thermal properties. A comparison with the macroscopic data finally demonstrates that photorefectance microscopy is a powerful tool to interpret, quantitatively, the microscopic origin of the macroscopic thermal properties of these C/C-SiC composites.

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# **Interphases/coatings**

**Tuesday, October 2<sup>nd</sup>**  
**Morning session**



## **Oxide Fiber-Coatings for Interface Control in Ceramic Composites**

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Keywords: coating, oxide, interface, interphase, pullout, fracture

There has been significant recent progress in the development of new fiber coatings to promote crack deflection and distributed damage mechanisms in ceramic composites. There is now definitive proof that oxide coatings can provide good composite behavior in real composites. Examples will be summarized and discussed. The evaluation of oxide based approaches required developing viable coating processes and solving pervasive problems with fiber degradation. This infrastructural overhead has required substantial effort and has only recently been accomplished sufficiently to allow evaluation of new coatings in actual yarn reinforced composites. The role and status of this part of the problem will also be summarized. Remaining issues and future research needs will be discussed.

## Interphase Formation, Microstructure and Performance

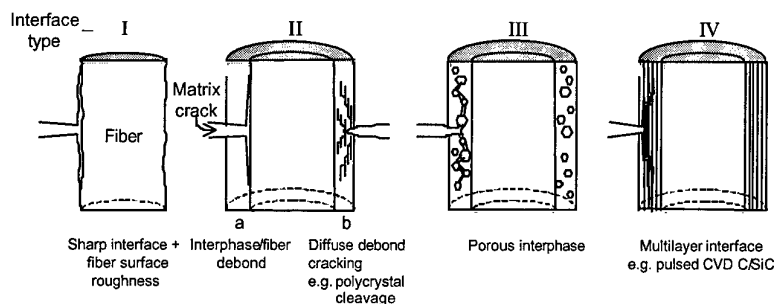
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**Keywords:** Interface, Debond-energy, Fiber-coating, Oxidative-stability, Composite-failure.

The essential property of a fiber-matrix interface in brittle-matrix CMCs is the ability to 'debond' in the path of transverse matrix microcracks. This is the key to toughness and damage-tolerance, resulting in a characteristic non-linear stress-strain response during progressive load-transfer to the high strength aligned fibres which have a comparatively high failure strain. The design of an ideal interface requires a control of debond energy relative to fiber fracture-energy together with the shear stress for the debonded interface. These parameters together with elastic properties, relative dimensions of fibre and matrix and residual stresses, determine the matrix cracking threshold relative to ultimate fibre/composite failure stress. In addition to these micromechanical parameters the interface must be thermodynamically compatible with fibre, matrix and environment and also be introduced into the composite microstructure via convenient synthesis and fabrication procedures.

The fabrication constraints, together with the need to control interface debond and shear parameters has evolved a series of interface types which depart from the simplistic description of a sharp discontinuity between the fibre and matrix phases. The interface is generally a zone of finite thickness (the interphase) with varying composition and microstructure, produced either by natural processing reaction or by fiber pre-coating, which exhibits differing debond mechanisms typified in Fig. 1.

Fig.1 Interface types with varying debond/shear mechanisms.



This paper, presents a review of interface types which have evolved for enhanced CMC performance over a range of temperature and identifies current limitations in their application to oxide and non-oxide systems. For example, the major constraint with carbon-rich interfaces is the low oxidation threshold which has been only slightly increased with the use of boron nitride. With a change to all oxide systems, attempts to replicate the weak cleavage behaviour of layered graphitic or BN crystallites have been inhibited by the difficulty in coating fibres with fine crystallites of hexaaluminates (such as hibonite and rare earth  $\beta$  aluminas) or layered phyllosilicates. The more recent attempts to provide intrinsically low-cohesion interfaces between oxide phases and complex tungstates, phosphates or vanadates (monazite and xenotime structures), have been inhibited by difficulties in the coating of fine fibres and the detrimental effect on fibre strength. There is also recent evidence that monazite/oxide interfaces may not have the ideal debond characteristics for lateral cracks in the absence of a critical level of porosity, which is a factor previously identified for  $ZrO_2$  interphases in  $Al_2O_3$ /saphikon CMCs.

It is concluded that the development of oxidation-stable interphases has reached a critical stage; novel microstructures and compositions together with simple coating procedures are vital ingredients for future HTCMC development and application.

## Experimental Investigation of Multifunctional Interphase Coatings on SiC fibers for Non-oxide High Temperature Resistant CMCs

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Keywords: ceramic interphase coatings, ceramic fibers, oxidation resistance.

Multifunctional interphase coatings are necessary constituents of nonoxide CMC in order to provide high fracture toughness and the protection of the reinforcing fibers from oxidation. Two-layer coatings could hypothetically fulfill these functions. For example, a dense highly oxidation resistant layer on the fiber surface covered by a friable over-layer, which may not only provide weak matrix bonding but also protection of the fiber and its first coating at high temperatures.

Experimental investigation of a two-layer coating was carried out using Hi-Nicalon fiber and two ceramic coating layers: the first, a CVD layer of Mo-Si structure, and the second, a Si-B-C-N structure formed by the pyrolysis of a polymer precursor. It was established that the Hi-Nicalon fiber tested at 1300 – 1500 °C in air between 20-50 hours undergoes negative surface changes; that is, a layer of SiO<sub>2</sub> with thickness about 0.5-0.8 micron is formed, having appreciable cracks along and across the axis. So the fiber really needs improved protection. Both coating layers were put by CVD and PIP technology accordingly at the temperatures not higher than 1000 °C and had a thickness of about 0.1-0.3 micron. Testing of analogue materials in air showed noticeable protective action of individual and combined coatings. The SiO<sub>2</sub> layer was a little thinner and had no cracks. At the same time, both coatings were dense with good adhesion to fiber and to each other. So even being very thin they lowered the RT strength of the fiber as coated to 60-65 % of its initial value.

These results were analyzed on the base of the "interaction of brittle fibers with brittle layers" theory and fractographic study. The impossibility of aligning dense high modulus high strength layers directly to the fiber surface and the necessity to make Si-B-C-N structure more friable followed from the analysis. This led to a three-layered coating structure. The first layer should be a buffer coating. It ought to determine the adhesion between the fiber and the protective coating, being very uniform and oxidation resistant; but having rather low axial shear strength. The second layer - the really protective layer - should be dense, of high modulus, and as oxidation resistant as possible. Its compatibility to the fiber with regard to the coefficients of thermal expansion is not required probably to be ideal. The third layer should control the adhesion between the coated fiber and the matrix and be friable, displaying plasticity at high and low temperatures. The materials of current interest are Ti<sub>3</sub>SiC<sub>2</sub> for the buffer layer, MoSi<sub>2</sub> for the second layer, and (SiC+ Si-B-N-C) for the third layer.

## Coating of SiC-Fibers with Yb-doped Ceria

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**Keywords:** SiC fibers, Yb-doped ceria, Mullite-alumina matrix, Hot-pressing

In a previous work, ceria was coated on the surface of alumina fibers to avoid the sintering between the fibers and alumina matrix. No chemical reaction in air was observed in the X-ray diffraction patterns for the alumina-ceria system below 1500 °C. Furthermore, it was found that in the alumina-silica-ceria system,  $\alpha$ -alumina, mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ) and ceria coexisted below 1500°C. That is, ceria can be expected as a chemically inert interphase in the composite of alumina-silica-ceria system. However, the grain growth in the alumina fibers and ceria layers, which increased the roughness at the interfaces, caused the brittle fracture of the composite. Suppression of grain growth in the interface layer and fibers is required to lead the pull out effect of fibers. Doping rare-earth element into ceria suppressed the grain growth.

In this paper, Yb-doped ceria with composition of  $\text{Ce}_{0.8}\text{Yb}_{0.2}\text{O}_{1.9}$  was used to coat SiC fibers by solution immersion route using  $\text{Ce}(\text{NO}_3)_3$  and  $\text{Yb}(\text{NO}_3)_3$ . The alumina fibers were replaced by high-strength SiC fibers to suppress the grain growth and degradation during the processing. The phase compatibility between the fibers and coating layer was studied in Ar atmosphere and in air at 1100-1300°C. The heat-treatment of the mixture of Yb-doped ceria/SiC fibers containing Al sintering additive (<1 mass%) in Ar atmosphere at 1300°C produced  $\text{CeAlO}_3$  and  $7\text{Ce}_2\text{O}_3 \cdot 9\text{SiO}_2$ . Subsequent heating of the fibers in air at 1100°C decomposed  $\text{CeAlO}_3$  and  $7\text{Ce}_2\text{O}_3 \cdot 9\text{SiO}_2$  into  $\text{CeO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ . The SiC fibers coated with Yb-doped ceria and 80 mass% mullite- 20 mass% alumina sheets of 75  $\mu\text{m}$  thickness, which were formed by doctor blade method, were laminated and hot-pressed at 1200°C in Ar atmosphere. As hot-pressed composite with 15 vol% fibers and the composite subsequently heated in air at 1100°C showed ductile and brittle properties in the stress-strain curves, respectively. This result was associated with the phase stability at the interfaces between the fibers and matrix.

## Stability of Mullite-Precursors Versus Potential Fiber-Coating Materials

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Keywords: mullite-precursor, fiber-coating, interfacial reactions

Damage tolerant all-oxide ceramic matrix composites (CMCs) with dense, mechanically strong matrices require the development of a suitable fiber/matrix-interfaces which provide fiber/matrix debonding and crack deflection. This interface can be provided by a thermodynamically stable oxide fiber coating. Oxide/oxide CMCs intended for application as HT-structural materials are usually fabricated from mullite-based fibers and mullite matrices, mainly due to the favorable high temperature properties of mullite. The mullite-matrices are commonly produced from highly reactive, diphasic  $\text{SiO}_2\text{-Al}_2\text{O}_3$  precursors, which can easily react with other metal oxides, forming stable  $\text{SiO}_2$ -rich glass phases. Therefore it is important, that oxide fiber coatings are stable against non-crystalline  $\text{SiO}_2$  during composite manufacturing, which normally is performed at temperatures up to  $1400^\circ\text{C}$ . Of special interest is the behavior of the fiber coating in its non-crystalline state, because it then displays a much more higher reactivity with silica. In this work, three of the most discussed fiber coating systems (Zirconia, La-Hexaaluminate and La-Monazite) are evaluated with respect to their stability in mullite matrix composites. Precursors of the examined coating materials were synthesized by solution-precipitation or sol-gel processes. Laminates of mullite and the respective coating materials were fabricated by hot-pressing of stacked mullite precursor and coating precursor powders at  $1400^\circ\text{C}$ . The interlaminar interfaces were examined by microstructural analyses. The experiments showed that interfacial reactions can be avoided by careful control of chemistry and crystallization behavior of the coating materials.

## Microscopic thermal characterization of C/C composites

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**Keywords :** C/C composites, carbon fibers, pyrocarbon matrix, morphology, photoreflectance

Both carbon fibers and matrix of C/C composites (figure 1) are made of graphite nano-elements that are individually thermally very anisotropic. Their texture strongly influence the thermal properties of these constituents and consequently the behavior of the composite itself /1/. Thus precise determination of fibers and matrix microscopic thermal properties, often not precisely known, is fundamental to improve the performance of the composite. Since several years, photoreflectance microscopy have demonstrated its capability to measure the thermal properties of complex materials at a microscopic scale /2/3/. But, additional efforts are necessary to into account the strong thermal anisotropy of graphite so as its morphology/4/.

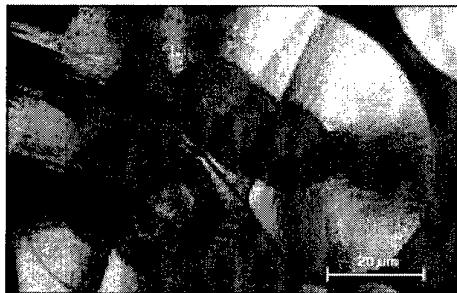


Figure 1: Micrograph of a C/C composite showing the position and dimension of the fibers and matrix to characterize.

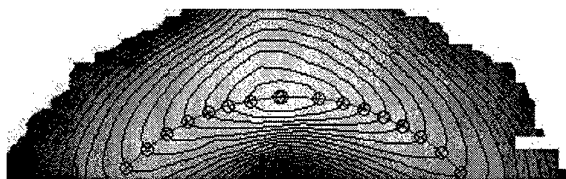


Figure 2: Phase of the periodic temperature increase field (10  $\mu\text{m} \times 6 \mu\text{m}$ ) in a pyrocarbon matrix measured by photoreflectance microscopy outlining the thermal anisotropy of the material and the curvature of the graphitic plane.

At first we detail photoreflectance microscopy technique principles and performances. Then, results of microscopic heat diffusion measurements in various types of carbon fibers (pitch, PAN and rayonne) are presented that are in good agreement with their known structure. Then, different varieties of pyrocarbon matrix are analyzed with a rigorous thermal parameters extraction scheme, in order to determine precisely the thermal anisotropy and diffusivities of the matrix. The results, that are compared with morphologic observations by polarized light microscopy, outlines the influence of the process parameters on the evolution of the local thermal properties of the matrix. To conclude perspectives concerning fiber/matrix interfaces characterization, using this technique, is presented. This study demonstrates that photoreflectance microscopy is a powerful tool to measure quantitatively the various microscopic parameters influencing the macroscopic thermal properties of the composite.

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## **Fibre induced failure of Carbon/Carbon Composites**

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A handicap of C/C composites is the low strength down to only 15% of the original carbon fibres. According to published knowledge initial matrix cracks develop under external load causing fibre failure. Consequently weakening of the fibre/matrix interface would reduce fibre failure by crack deflection (mode II). But X-ray Refraction Analysis (SAXS) of C/C composites with differing fibre sizing shows clearly that the blocking of active groups at the fibre surface creates partial fibre debonding. The average interface shear strength is reduced because of the reduced bonding area. Thus matrix cracks still have a chance for fibre damaging. Therefor interface weakening is not the ultimate solution to the problem. By contrast the weakening of the C-fibres during pyrolysis of the precursor polymer is very probable. Wide Angle X-ray Scattering, Raman and LAMMA (Laser Microprobe Mass Analysis) investigations prove significant structural changes in correlation to the reduced strength at different treatment temperatures. Crystal damaging by highly reactive hydrogen and other chemical contamination are proved. The weakened fibres cause failure of the composite.

Keywords: C-fibre degradation, fibre debonding, fibre induced failure, X-ray Scattering

## The Interlaminar Shear Strength of C/C-SiC

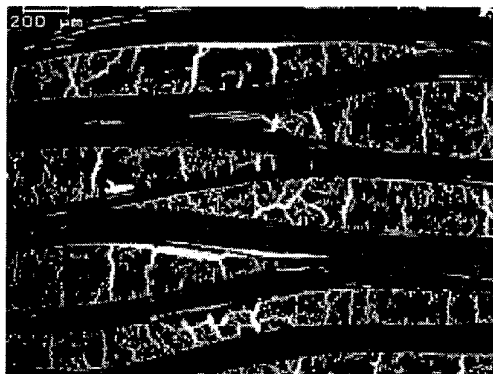
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**Keywords:** characterisation, LSI-process, ILSS, adhesion, double notch compression shear test

C/C-SiC is a pyrolytically produced carbon fibre reinforced carbon (C/C) that has been infiltrated with liquid silicon after the initial pyrolysis. Silicon reacts with carbon from both matrix and fibres in the areas of the former shrinkage cracks thus producing a nearly dense ceramic matrix composite.

The degradation of fibres coming into contact with silicon is a problem, that is mainly influenced by the crack pattern. Its development is governed by the adhesion between fibres and polymeric matrix. Using C-fibres as delivered by the manufacturer leads to a high adhesion in all states (CFRP, C/C, C/C-SiC) due to the prior oxidation pretreatment. This results in a dense microstructure of C/C-segments surrounded by SiC. During siliconization only few fibres degrade, but the adhesion in the segments is too high for a damage tolerant behaviour. To reduce adhesion a thermal fibre pretreatment (TFP) of the fibres under inert atmosphere is used. The microstructure of these materials is dominated by inner-segment cracks (see figure) leading to a higher amount of degraded fibres. In its extreme no segments can be found, nearly all fibres are siliconized, resulting in brittleness, too.



C/C specimen after pyrolysis up to 900 °C (fibre pretreatment temperature 600 °C, fluorescenscopic optical microscopy)

The focus on the presented work is on the intermediate state. Former research work demonstrated, that using medium temperatures in TFP result in a material in which on the one hand the non-degraded fibres lead to a certain damage tolerance, on the other hand the siliconization of the fibres can be limited so that the material exhibits good overall mechanical properties. Research work has been conducted to find out how the ILSS is influenced by TFP temperatures.

Experiments have been done with specimens that differ only in the TFP temperature. The primary objective was to establish the interlaminar shear strength (ILSS) using the double notch compression shear (DNCS) test (ASTM D 3846-94). CFRP-, C/C-, C/C-SiC have been tested. The correlation between ILSS and TFP temperature has been established. Further tests have been done with two different unidirectional materials produced with oxidised (high adhesion) and non-oxidised fibres (extremely low adhesion). The shear strength in this case depends mainly on the adhesion between fibres and matrix. It was found, that ILSS and adhesion behave similar during pyrolysis.



## **Stability of BN coatings processed from the (BCl<sub>3</sub>, NH<sub>3</sub>, H<sub>2</sub>) gas mixture at ambient temperature**

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The control of the BN stability is important for the processing of CMCs with BN interphase to limit the ageing of the interphase, even at ambient temperature and so the deterioration of the properties of the composites.

BN coatings were processed by CVD from the (BCl<sub>3</sub>, NH<sub>3</sub>, H<sub>2</sub>) gas mixture at low pressure and temperature. In common processing conditions, the coatings are amorphous. The crystallisation of these coatings requires a post-deposition heat treatment. The stability in air at ambient temperature of the coatings before and after heat treatment was studied through : (i) the weight gain as a function of time (from few days to 2 months), (ii) the quantity of oxygen or moisture absorbed (measured by AES), and (iii) the characterisation of new compounds at the coatings surface by XRD. The oxidation resistance of the aged coatings was evaluated by TGA and results were correlated with the quantity of oxygen absorbed. The crystallisation degree (characterised by the inter-reticular distance and width at mid-peak height) of the aged coatings after heat treatment was also related to the quantity of oxygen present before the heat treatment. AES analyses performed immediately after heat treatment revealed that oxygen was still present, although the volatilisation of oxygen bearing species during the heat treatment was detected by mass spectrometry. Thus, the influence of the presence of oxygen in BN coatings before the heat treatment on the crystallisation is highlighted.

## **Oxidation resistance of BN coatings with different textures**

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Non-linear stress-strain behaviour of CMCs results from the multiple microcracking of the matrix and crack deflection into the fibre-matrix interfaces. This phenomenon can be controlled through the deposition of a layer of a soft material on the fibre surface prior to matrix infiltration. Boron nitride has often been suggested as an alternative to anisotropic pyrocarbon in various composites SiC/SiC for service at elevated temperatures in oxidising atmospheres. There is indeed a marked similarity between BN and carbon. Further, BN displays an unusual combination of properties including thermal stability, corrosion resistance and mechanical properties. The lifetime, at temperatures less than 1100°C, of these composites depends mainly on the oxidation behaviour of the BN interphase. The knowledge of its resistance against oxidation is necessary and must be related to its crystallographic parameters. BN layers were deposited from different gas mixtures ( $\text{BF}_3$ ,  $\text{NH}_3$ ,  $\text{H}_2$ ) or ( $\text{BCl}_3$ ,  $\text{NH}_3$ ,  $\text{H}_2$ ). The microtexture of coatings is controlled by the evolution of the processing conditions. Oxidation resistance of these coatings is discussed in terms of : (i) degree of crystallisation, (ii) texture (extension and orientation of coherent domains) and (iii) deposition mechanisms depending on the gas precursor. This discussion was made possible by considering coatings deposited on different substrates, presenting more or less proportions of (002) planes edges on their surface (sides of crystallites being the most sensitive to oxidation).

## CVD-Coating of Fabric Sheets in Combination with the LSI-Process

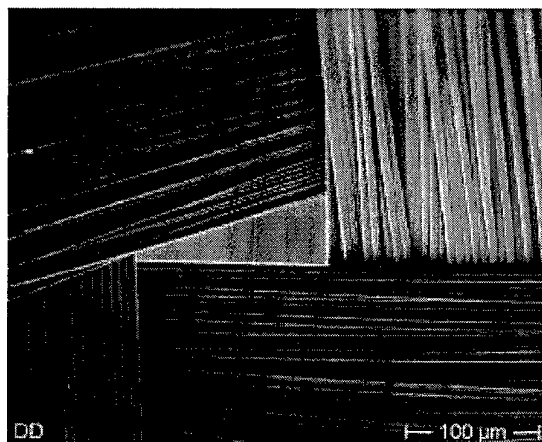
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**Keywords:** CVD-coating of C-fabrics, characterisation, LSI-process, microstructure

Due to short processing times and fairly low manufacturing costs the Liquid Silicon Infiltration Process (LSI) developed at the DLR in Stuttgart is a well established process to produce ceramic matrix composites without any fibre coating. The key step is the liquid silicon infiltration of porous carbon/carbon composites (C/C) whose distinct microstructure is built in the preceding pyrolysis step of carbon fibre reinforced plastics. Those were produced by resin transfer moulding (RTM) in a first step. This process leads to C/C-SiC composites being characterized by high mass-specific properties in combination with an extreme thermal shock stability. Applying special process parameters the microstructure as well as the physical properties can be tailor-designed to match specific requirements. However, C/C-SiC has a low damage tolerance compared to CMCs reinforced with coated fibres. Unfortunately, single fibre coating increases CMC costs considerably.

In order to overcome this problem, C-fabrics shall be coated with pyrolytic carbon (pyC) and then submitted to the LSI-process yielding dense C/C-SiC. In a first step, C-fabric sheets (30 mm in width and 300 mm in length) were coated with pyC in a CVD-cold-wall reactor under static conditions at about 1000 °C. Toluene was used as a precursor whereas argon served as a carrier gas. Deposition times ranging from 5 to 20 min resulted in an increase in weight of 64 to 200 mg corresponding to a mean layer thickness of 49 to 150 nm on each single fibre.



SEM micrograph of uniformly coated C-filaments with pyrolytic carbon.

The pyC-coated C-fabrics revealing increased stiffness with increased coating thickness as well as reference samples were submitted to the conventional LSI-process. The resulting CMCs are characterized by microscopy, and the mechanical properties of these new kind of materials as well as the intermediate products are reported. While the samples with coated fabrics showed failure in shear, the reference samples revealed catastrophic failure in short beam bending tests. Consequently, the damage tolerance of C/C-SiC could be improved by coating C-fabrics.

## Mechanical Properties of SiC/SiC Composites with ZrSiO<sub>4</sub> Interphases at a High Temperature

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Keyword: CMC, ZrSiO<sub>4</sub>, polymerized complex

The development of interphase for protecting the fibers during services in corrosion environments at elevated temperatures is necessary for fiber-reinforced composites to be used in critical applications. Carbon was the most commonly used interphase in the past. BN interphase has the problem of the stability in oxygen- or water- containing environments. ZrSiO<sub>4</sub> has excellent stability for the SiC fiber and carbon up to 1600°C. ZrSiO<sub>4</sub> interphase, which is a new interface material, was prepared by the polymerized complex technique method. The polymerized complex technique was useful technique for the molecular-scale mixing of cations in any materials. The citric acid-ethylene glycol solution containing Si and Zr ions was polymerized at 130°C to obtain a polymerized complex precursor. A single tow of Si-Zr-C-O (Tyranno® ZMI fiber) fiber was dipped into this precursor. Heat-treatment was conducted at 500°C for 1hr in air. ZrSiO<sub>4</sub> interphase was prepared by repeating these operation by a few times. In order to compare this new interphase with carbon and BN interphases which were prepared by CVD, Si-Zr-C-O fiber /SiZrC which had ZrSiO<sub>4</sub>, carbon or BN were fabricated by PIP (Polymer Impregnation and Pyrolysis), and mechanical properties of these minicomposites at a high temperature were evaluated. The minicomposites with carbon interface showed lower tensile strength above 1000°C in air. Even the minicomposites with BN interphase showed lower tensile strength above 1200°C in air. On the other hand, the ZrSiO<sub>4</sub> interphase showed higher tensile strength up to 1300°C in air. From the observation of microstructures of the minicomposites with ZrSiO<sub>4</sub> interphase, it was found that fiber was protected by the ZrSiO<sub>4</sub> interphase.

## Multiscale investigation of the creep behaviour of SiC<sub>f</sub>-SiBC composites

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**Keywords:** creep, interfaces, interphases, damage mechanics, TEM and HREM

Tensile creep investigations under argon were performed on SiC<sub>f</sub>-SiBC composites in the 1273-1673K temperature and 120-200 MPa stress domains. These composites have a self-sealing multi-layered matrix made by different chemical vapor infiltrations. They were reinforced by Nicalon NLM 202 or Hi-Nicalon SiC<sub>f</sub> fibers.

These materials present a good creep resistance  $10^{-8}$ - $10^{-9}$ .s<sup>-1</sup>, in a temperature domain where super-alloys or un-protected materials are not working. It is only the use of the damage mechanics which can explain their creep behavior. That is, of course, supported by microstructural observations, where many brittle damages are observed: matrix microcracks, fiber/matrix debonding, microcrack deviations by fiber/matrix or matrix layer/matrix layer interfaces, fiber or yarn pull-out, fiber or yarn fractures, ....

By transmission and high resolution electron microscopies, the microstructure of these composites has been wholly described. Evolution of the different matrix layers and of the interfaces and interphases during creep has been followed as a function of temperature and stress, as they play a major role on the thermomechanical behavior of such materials, and particularly on the development of the matrix microcrack arrays. In fact observations at different scales have allowed to evidence the role of the turbostratic carbon planes acting as mechanical fuses and as a deviation agent for the matrix crack propagation.

With the help of the macroscopic results, the multiscale observations, the morphological damage quantification, the different involved micromechanisms, the components which govern the creep strain of the SiC<sub>f</sub>-SiBC composites have been proposed as a function of the test conditions and also a mechanism.

## Evaluation of damage by oxidation corrosion at high temperatures of coated C/C-SiC ceramic composite

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**Keywords:** coating, oxidation, ageing test, thermo-gravimetric analysis, cracks, loss of weight

The application at high temperatures in oxidising environments of industrial components manufactured by carbon long fibre reinforced ceramic composites, as tubes and plates for high temperatures heat exchangers, requires effective protection systems to avoid internal fibers and free C oxidation and a significant reduction of the strength and lifetime of the component.

This type of material is generally internally cracked with not negligible open porosity so it requires an external coating protection to avoid oxygen diffusion and internal corrosion.

Some multilayers coating systems are in a developing phase, trying to seal the basic SiC coating crack opening at the critical temperatures by additional glassy phases activated by the presence of additional layers as alumina, boron carbide, mullite, etc.

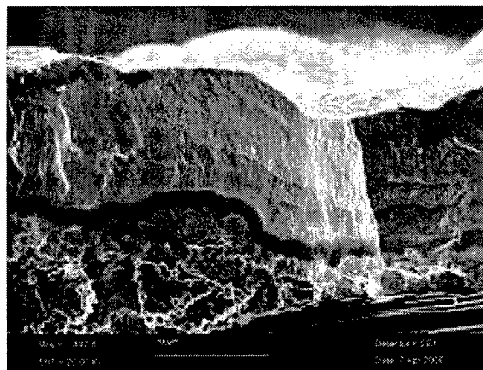
In the framework of some European BRITE Projects, oriented to the development of CMC materials oxidation and corrosion resistant, an experimental activity was set up and performed to evaluate the effectiveness of some coating systems developed by performing ageing tests and evaluating the change of some basic properties of the material.

Many standard flat and some tubular samples of the same bulk material, C/C-SiC 2D 1/2 carbon cloth based with 0-90° fibre orientation, coated with different coating systems were aged in static air at different temperatures for different times, measuring the change of weight and the decrease in the ultimate strength, by four point bending tests or compression tests on C-Rings, at room temperature.

A microstructural analysis by optical and SEM microscopy was performed on some samples to evaluate the internal oxidation corrosion, the presence of cracks on coating and the formation of glassy phases.

Moreover a set of short time thermo-gravimetric analysis were performed on small samples of the same material, SiC coated, at different temperatures, in air or pure oxygen, with heating up and cooling down by inert gas protection, to evaluate the pure steady state oxidation effects.

The main results achieved up to now indicate that some multilayers coating systems decrease significantly the strength reduction of the CMC due to the oxidation applying a valid protection and can be considered a good basis for further developments



*Multilayer coating*

## **Chemical Vapor Deposition for Thermal and Environmental Barrier Coatings**

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**Keywords:** thermal barrier coatings, environmental barrier coatings, chemical vapor deposition, zirconia, yttria-stabilized zirconia, mullite

A current technology for thermal barrier coatings (TBCs) for high-performance turbine blades utilizes electron-beam physically vapor deposited (EBPVD) yttria-stabilized zirconia (YSZ). The deposits are columnar in nature, resulting in excellent strain tolerance during thermal cycling. There exist, however, a number of issues with regard to long-term stability and environmental degradation of these coatings. In the current work, a chemical vapor deposition process for YSZ is being developed for consideration as a replacement for EBPVD, as a supplement to EBPVD to coat regions that the line-of-sight process cannot reach, and as a seal coat for EBPVD layers.

Silicon carbide-based composites and silicon nitride materials are of substantial interest for gas turbine engine hot-section hardware due to their retention of strength and toughness at high temperatures. However, these materials suffer from recession due to high-temperature attack by high-pressure, high-velocity water vapor and corrosive attack from alkali species. Environmental barrier coatings are thus needed to protect these materials from accelerated oxidation in water vapor and alkali contaminants. It has been observed that mullite coatings are protective of silicon-based materials in simulated combustion environments. A CVD process for fabrication of thin, dense, high-purity mullite coatings has been developed and numerous oxidation tests have confirmed phenomenal protective capacity in high-temperature, high-pressure water vapor, as well as in exposure to alkali species.

## Environmental Barrier Coatings for Silicon-Based Ceramics

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The key factor that limits the performance of current gas turbines is the high temperature capability of structural components in the engine hot section, such as blades, nozzles, and combustor liners. Ceramics in general exhibit superior high-temperature strength and durability, implying their potential application in the hot section of gas turbine engines. Silicon-based ceramics, such as SiC fiber reinforced SiC (SiC/SiC) ceramic matrix composites (CMC) and monolithic silicon nitride ( $\text{Si}_3\text{N}_4$ ), are prime candidates for such applications. However, silicon-based ceramics suffer from rapid surface recession in combustion environments due to the volatilization of silica scale via reaction with water vapor, a major product of combustion. Molten salts in combustion environments also attack silica scale, causing catastrophic failure of silicon-based components. Therefore, successful commercial application of silicon-based ceramic components in the hot section of advanced gas turbine engines requires development of a reliable method to protect the ceramic from environmental attack. External environmental barrier coating (EBC) is a logical approach to achieving protection and long-term stability.

EBCs based on mullite and YSZ were developed in early 90's with their main focus on protection from molten salt corrosion. The mullite-based EBCs were the baseline coatings upon which more advanced EBCs with dramatically improved performance were developed in the High Speed Research-Enabling Propulsion Materials (HSR-EPM) Program in a joint effort between NASA, General Electric, and Pratt & Whitney. The new EBCs consist of three layers, a silicon bond coat, a mullite ( $3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$ ) or a mullite+BSAS ( $\text{BaO}_{1-x}\text{-SrO}_x\text{-Al}_2\text{O}_3\text{-}2\text{SiO}_2$ ) intermediate coat, and a BSAS top coat. The EPM EBC was scaled up and successfully applied on Solar Turbine gas turbine engines under DOE-CSGT Program. This presentation will discuss the development and characterization of EPM EBCs.



## New application of a thin $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ composite as surface protective material for brittle materials

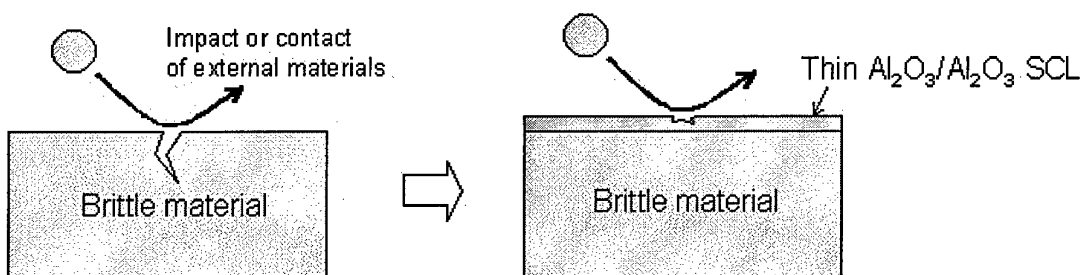
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**Keywords:** Protective layer, Surface composite layer (SCL), DCB specimen,

Engineering materials are exposed to various environments such as thermal, corrosion, erosion and foreign object impact, when they are applied in service condition. Therefore, environmental barrier coatings (EBC) are required to maintain a safe life of components and structure. However, most of protective layers, which is made of oxide ceramics, are easily cracked by mechanical damages and lost their functions as a protective layer, even though they are a good protective layer for the thermal damage and oxidation.

Figure 1 The concept of a protective layer using the SCL.



To protect a material from mechanical damages as well as chemical damages, we have proposed a thin oxide/oxide composite, especially woven fabric  $\text{Al}_2\text{O}_3$  fiber-reinforced  $\text{Al}_2\text{O}_3$  matrix composite,  $\text{Al}_2\text{O}_3/\text{Al}_2\text{O}_3$ , as a protective layer because of its high damage tolerance, notch insensitivity and inherent oxidation-resistance (Figure 1). To realize the application, it is necessary to understand the mechanical properties of SCL/substrate interface for optimizing the effectiveness of EBC and the capability of mechanically protective coating.

The aim of this study is to examine the advantage of the SCL. The effect of adhesion strength on the advantage is also discussed. The indentation test was performed to introduce damage to the specimen. Then bend strength was obtained with the specimen carried out the indentation test. Through these sets of results, the potential of SCL is discussed.

## Yttrium-Silicates for Oxidation Protection of C/C-SiC Composites

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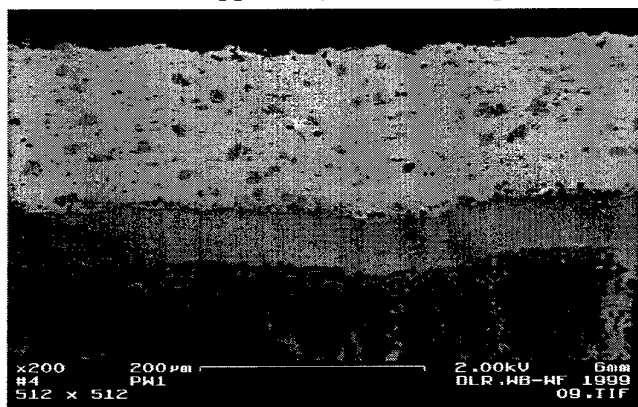
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**Keywords:** coating, multi-layer, oxidation protection, plasma-spraying, yttrium-silicates

Hot structures designed of carbon fiber reinforced ceramic materials like C/C or C/C-SiC are key technologies for applications of light weight thermal protection systems (TPS) of reusable hypersonic aerospace vehicles. All these materials combine the high temperature capabilities of carbon and/or silicon carbide with the benefits of fiber reinforcement. However oxidation sensitivity of carbon fibers above 400°C is the limiting factor for the use of such composite materials under atmospheric reentry conditions. Therefore oxidation protection coatings are inevitable in terms of reliability of structural C/C or C/C-SiC components. Currently used coating systems consist of several layers (multi-layer) with different materials, each designed to perform a specific function. Advanced multi-layers have to proof adequate erosion resistance as well as effective self-healing properties at temperatures up to 1600°C. Furthermore the coating technique itself has to support both applicability on large structural parts with complex geometry as well as repair procedures of possibly damaged surface areas after the first flight.

In this study an effective two-layer coating system on C/C-SiC has been developed (figure) which consists of SiC applied by chemical vapor deposition (CVD) and a dense layer of yttrium-silicate



with inlays of amorphous silica applied by low pressure plasma-spraying (LPPS). The coating was qualified on C/C-SiC specimens by several test campaigns in plasma wind tunnels at temperatures between 1350°C to 1650°C and pressure regimes of 3 and 75 mbar. After a test duration of more than 20 minutes at 1600°C the visual appearance of the coating did not change significantly. Thus the specific mass loss rates are very low. The thermal shock resistance was proofed by tests within a solar furnace with the result of a very

good adhesion to the bonding layer of SiC. Due to low oxygen permeability of the silicate and the thermo-viscous behavior of the silica inlays, further expensive sealing layers are not required.

The used installation for low pressure plasma spraying is well suitable for coating on structural parts with curved contours or braces. It is equipped with a computer-guided robot system for the movement of the plasma torch inside a chamber that allows the deposition of substrates up to 1 m<sup>2</sup>. After successful qualification of samples protected by the new coating system, the current work is now focused on upscaling the LPPS technique on larger C/C-SiC components of TPS systems.

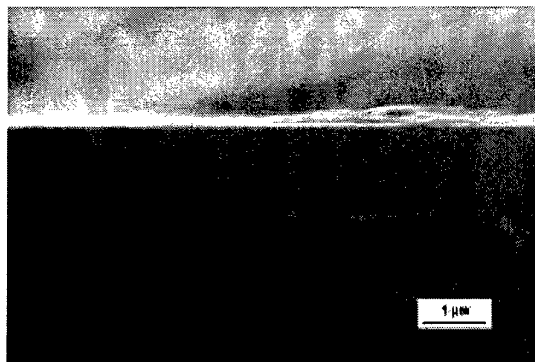
## Polymer-spraying as a deposition technique for CMCs

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**Keywords:** Si-polymer, precursor, spraying, coating

Silicon based preceramic polymers have been synthesized to produce coatings, bulk materials, ceramic fibers and ceramic matrix composites (CMC) with outstanding properties. Many sumptuary technologies has been developed to handle different kinds of organometallic precursors. However, due to the inevitable shrinkage during the pyrolysis process at about 1000°C, an open porosity could not be prevented. This is a disadvantage for the most engineering applications under possibly aggressive conditions at high temperatures. Especially the composite materials have to be protected to prevent early breakdown.

We developed this novel shaping technology in order to coat fibers as well as the compact sample with an dense and crack-free amorphous coating. The applied metalorganic polymers vary from commercial polysiloxanes (which can be easily handled in air) to non-oxide precursors like polysilazanes. A solution or suspension can be produced by adding a reactive or an inert filler to minimize volume shrinkage and to improve the properties of the coating. Temperatures up to around 1000 °C under inert conditions were applied, resulting in amorphous SiOC or SiCN.



SEM-image of an amorphous SiCN-coating on a graphite substrate.

This technology gives us the opportunity to coat complex-shaped surfaces with an oxide or non-oxide coating of 0.2 to 2.5 µm without delamination or segmentation. It was found that different substrate materials could be coated successfully when no moisture was present at the surface. Especially carbon fibers, ceramic materials like alumina and several metals (silicon and some sort of steels) showed a good wetting behaviour resulting in dense and homogenous coatings. Typically, the surface roughness decreases, reaching values of 0.2 µm and less. SiCN coatings can be processed with oxygen contents as low as 4 wt% applying a nitrogen atomization and fast mirror furnace heating. This technology was established without the use of a glovebox.

The coatings can be used to improve the chemical stability and oxidation resistance and to prevent the composite material from corroding and, as a consequence, having better mechanical stability under extreme corrosive conditions.

## Protective coating for carbon carbon composites

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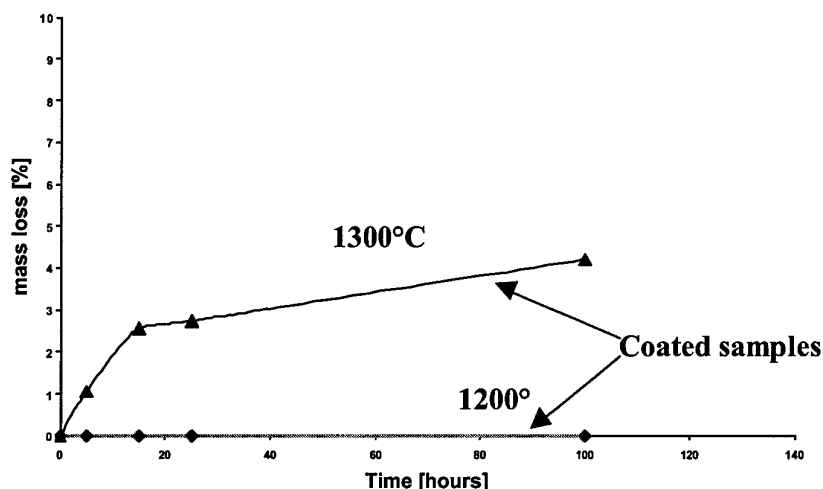
Oxidation-protective, multilayer coatings were deposited on carbon-carbon composites (C/C) by a simple and low cost slurry method. The chosen coating materials are glasses, glass-ceramics and composites.

The wettability of the glasses on the composite was promoted by the formation of a 5-10  $\mu\text{m}$   $\beta$ -SiC layer on the composite surface, by direct reaction of liquid silicon with the C/C.

The coating consists of two layers; the inner is composed by a barium borosilicate glass filled with boron carbide particles, the outer is formed by a mixture of the same glass and yttrium oxide. The layers are deposited by slurry technique (powdered coating material and ethanol) and the heat treatments were performed in tubular oven in inert atmosphere (Ar).

Measurements of oxidation resistance were carried out in a furnace in air. The C/C coated samples were submitted to heat treatment (thermal cycling) in order to verify the stability of the coating and its degree of protection.

No mass loss of the C/C composite was observed after 100 hours at 1200°C, while the fully coated C/C mass loss after thermal cycling (100 hours at 1300°C) did not exceed 4.2% (see fig 1). The efficiency and the easy maintenance of the coating is discussed.



**Fig.1. Oxidation tests on multilayer coated C/C**

## Low Cost Oxidation Resistant C-C Composites

J.C. Withers, W. Kowbel, and C. Bruce

Keywords: C-C Composites, Oxidation, CVR, Inhibition, Coatings

Carbon-carbon (C-C) composite exhibit excellent thermal, mechanical and chemical properties. Many commercial applications suffer from high manufacturing cost and poor oxidation resistance. A new process was developed to produce large (up to 1.5m x 1.5m), thick (up to 10cm) C-C composites in one step manufacturing, which can be processed out in one week or less. In addition, liquid based borosilicate inhibitors have been developed that are used as a component of the carbon matrix or added as a coating. Excellent oxidation resistance up to 750°C has been achieved via inhibition. Chemical vapor reaction (CVR) formed external SiC-B<sub>4</sub>C coatings have been developed which extended the oxidation resistance up to 1500°C. In addition, good mechanical (tensile strengths in excess of 200 MPa) and thermal conductivity (40 W/mK through the thickness, 300 W/mK in-plane) were achieved. Processing, mechanical properties, and oxidation data will be presented.

## Analysis of Asymmetrical Four-Point Bending Test of Ceramic Composite Joints By Using Finite Element Method

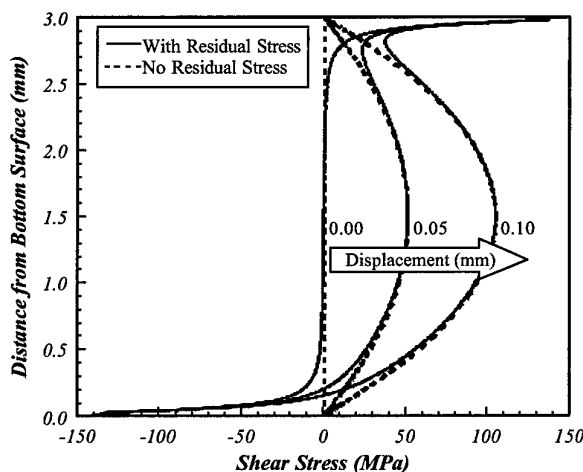
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**Keywords:** joining, shear strength, SiC composite, finite element method

As a result of R&D efforts, in the various types of joining between ceramic composite, an affordable, robust ceramic joining technology (ARCJoinT<sup>TM</sup>) has been developed as one of the most reliable method for the joining ceramics to use at elevated temperature. On the other hand, to establish useful design databases, the mechanical properties of joints must be accurately measured and quantitatively characterized. In many types of experimental techniques for measuring the shear strength of joints at high temperatures, an asymmetrical four-point bending test seems to be most economical due to the requirement of small test specimens with simple geometry. The shear stress of this test, however, has been evaluated according to the analytical method for homogeneous materials. Therefore, in this paper, the stress distribution under the asymmetrical bending test of SiC/SiC composites joined by ARCJoinT<sup>TM</sup> was precisely examined by using finite element method and the effects of the residual stress and the joint thickness were also studied.



Shear stress changes with and without the residual stress on the interface.

In the case without the effect of the thermal residual stresses, the calculated shear stress distribution at the interface between the substrate and the joint almost agreed with the analytical theory. In contrast, although the residual stress did not affect the predicted shear stresses at mid-plane of specimen width under the asymmetrical bending test, the calculated residual shear stress near the surface was very large and the possibility of an initial crack induced by the residual stress was considered. The effect of maximum temperature during the fabrication process on the residual stresses, however, was found to be small. Moreover, the effect of the joint thickness on the shear stress at middle of specimen width on the interface was found to be small, but the residual stress distribution near the surface was significantly affected.

## Thermal expansion and phase transitions up to 850°C of a Celsian-Hexacelsian mixture

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**Keywords:** Celsian-Hexacelsian, X-ray diffraction, high temperature

Four polymorphs of  $\text{BaAl}_2\text{Si}_2\text{O}_8$  are well known: celsian, paracelsian,  $\alpha$ - and  $\beta$ - hexacelsian. Monoclinic celsian, a framework aluminosilicate of the feldspar group [1], is the thermodynamically stable phase under ambient conditions. The less common mineral paracelsian converts to celsian on heating. Whereas the hexagonal  $\alpha$ - polymorph of hexacelsian is stable at room temperature, the orthorhombic  $\beta$ - modification stable above 300°C and another hexagonal, high temperature ( $\gamma$ -) phase stable above 700°C were confirmed recently by electron microscopy [2]. Hexacelsian was identified as one of the materials with displacive phase transformation which show potential use as transformation weakeners for debonding in  $\text{BaAl}_2\text{Si}_2\text{O}_8/\text{Al}_2\text{O}_3$  composites [3].

In order to investigate the thermal properties of potential celsian-hexacelsian composites, we performed high temperature X-ray powder diffraction of an intrinsic two phase mixture of 77 weight % celsian and 23 weight % hexacelsian, respectively. Experiments were performed on a STOE powder diffractometer using strictly monochromatic  $\text{MoK}_{\alpha 1}$ -radiation. A STOE furnace supplying capillary sample geometry allowed to collect high quality texture free data at elevated temperatures up to 850°C. Quantitative data analysis was performed using two-phase Rietveld refinement.

Two, hitherto unknown phase transitions were found in celsian: a first order transformation around 400°C with a volume change of 0.034 % and a second order transformation around 650°C. The volume thermal expansion changes from  $0.91 \cdot 10^{-5}/^\circ$  between room temperature and 400°C to  $1.03 \cdot 10^{-5}/^\circ$  between 400°C and 650°C and to  $1.46 \cdot 10^{-5}/^\circ$  above. Detailed anisotropic thermal expansion of the respective cell dimensions will be given.

Analysis of the hexacelsian minority phase confirmed the first order transition around 300°C and the second order transition around 700°C [2]. Volume thermal expansions of  $1.93 \cdot 10^{-5}/^\circ$ ,  $1.78 \cdot 10^{-5}/^\circ$  and  $2.04 \cdot 10^{-5}/^\circ$  were found for the  $\alpha$ -,  $\beta$ - and  $\gamma$ -phases, respectively. Anisotropic thermal expansion of the respective cell dimension will be given here also.

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[3] Shull J. L., *An investigation of several „transformation weakeners“ for ceramic composite inter-phases*, Ph. D. thesis, The University of Illinois at Urbana-Champaign, (1997)

## **Thermal Conductivity of Ceramic Coating Materials Using a Laser Heat Flux Technique**

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**Keywords:** ceramic coatings, thermal conductivity, silicates, laser technique

Thermal barrier and environmental barrier coatings have been developed to protect metallic and SiC-based ceramic components in gas turbine engines from high temperature attack. Zirconia-yttria based oxides and BSAS/mullite based silicates have been used as the coating materials. In this study, thermal conductivity values of hot-pressed zirconia- and BSAS/mullite-based coating materials were determined at high temperatures using a steady-state laser heat flux technique. During the laser conductivity test, uniformly distributed heat flux from a high power laser was delivered to the specimen surface to provide specimen surface heating. One-dimensional steady-state heating was achieved by using thin disk specimen configuration (25.4mm in diameter and 2-4 mm in thickness) and the appropriate backside air-cooling. The temperature gradient across the specimen thickness was carefully measured by two surface and backside pyrometers. The thermal conductivity values were thus determined at high temperature as function of temperature based on the one-D heat transfer equation. The radiation heat loss and laser absorption corrections of the oxide/silicate materials were considered in the conductivity measurements by evaluating the materials total emissivity and reflectivity. The effects of specimen porosity and microstructure changes on measured conductivity values were also evaluated. The high temperature thermal conductivity data are of great importance for future coating design.



## **Oxidation Behavior of C/SiC Composites with a Si-Zr Coating from Room Temperature to 1500°C**

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**Keywords:** Oxidation, C/SiC composite, Coating

As an oxidation protection coating, CVD SiC should be thick enough. Because the growth of a thick CVD SiC is extensive and unstable, it is impossible to remove preparation defects from the coating. Although the silica film formed on CVD SiC has an excellent oxidation resistance, it can not be used as a long-time coating. An outer layer is necessary to seal the defects of the CVD SiC coating. The outer layer should be completely dense and free of defects, and should be prepared by liquid method. Silicon, having a lower melting point and an excellent oxidation resistance, is a moderate outer layer material, but it is difficult to prepare a uniform silicon coating with an adequate thickness. However, silicides formed during the liquid preparation makes the outer layer more uniform and thicker. Mixtures of silicon and another metal may give better materials for the outer layer.

Three dimensional braid fiber preforms were used to fabricate the C/SiC composite by the low-pressure chemical vapor deposition method (LPCVD). Two kinds of specimens were machined from the prepared composite. The long specimens with a dimension of 4mm×5mm×140mm were used to investigate the oxidation behavior of the composite over the whole temperature range, and the short specimens with a dimension of 4mm×5mm×40mm were used to investigate the oxidation behavior of the composite at different temperatures. Both the long specimens and the short specimens were deposited for 20 hours to prepare a CVD SiC coating on the substrates after machining. A Si-Zr coating was prepared by liquid-reaction at 1500°C for 30 minutes on the SiC layer of the specimens. Oxidation tests in dry air were conducted in a furnace heated with MoSi<sub>2</sub> rods from room temperature to 1500°C. and in a combustion environment with a large temperature gradient from 300°C to 1300°C. Oxidation tests in combustion atmosphere with the flame temperature being 1250°C were conducted in a high-temperature wind tunnel which had a nozzle of 170mm in diameter by direct use of the long composite specimens. The specimens were held on the nozzle by fixing one end with bolts.

The oxidation behavior of a C/SiC composite with a Si-Zr coating in the range from room temperature to 1500°C could be described by a continuous series of functions relating weight change to temperature after oxidation for 5 hours. This model was used to explain different oxidation mechanisms at different temperature ranges. The oxidation was controlled by the reaction with a calculated activation energy of 28 Kcal/mol below 680°C, then by the oxygen diffusion through the matrix cracks from 800°C to 1000°C, and lastly by the oxygen diffusion through the oxide film formed on the coating surface with a calculated activation energy of 46 Kcal/mol above 1000°C. The resistance of the C/SiC was decreased with increase in oxidation time, and furthermore, the longer the oxidation time, the more rapidly the temperature at which the weight loss reached its maximum value was lowered and the maximum weight loss was increased. Below 1000°C, the strength and the weight loss of the composite changed with the oxidation temperature in the same manner, and reached their maximum values at almost the same temperature after oxidation for 10 hours. Above 1400°C, the composite lost strength as it gained weight. The displacements after oxidation in air and in the combustion atmosphere reached their maximum values separately at 600°C and at 700°C. The constant-temperature oxidation life of the coated composite at 1300°C in air was greater than 150 hours. In the preparation process of the coating, the pores between the fiber bundles were well infiltrated by the Si-Zr melt through the defects of the CVD SiC coating. In the oxidation process, ZrSi<sub>2</sub> grains formed, grew and arranged directionally in the pores.

# **Non-oxide CMCs: processing**

**Tuesday, October 2<sup>nd</sup>  
Afternoon session**

## **Applications of CMCs Made via the Liquid Silicon Infiltration (LSI) Technique**

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Keywords: ceramic matrix composites (CMC), processing, joining techniques, applications

Ceramic matrix composites (CMC) are very promising materials for use in structural applications when one considers their low mass, excellent thermal shock stability and strength at high temperatures. There are different processes for manufacturing complex shaped CMC components based on a fibre architecture of continuous carbon or silicon carbide fibres.

DLR in Stuttgart has developed the liquid silicon infiltration (LSI) process which allows the fabrication of thin walled, extremely lightweight C/C-SiC structures. It is a three step process starting with carbon fibre reinforced polymer (CFRP) manufacture followed by carbonization and concluding with liquid silicon infiltration.

The advantage of the LSI process is that it is a near net shape process without reinfiltration steps. Moreover, the LSI process enables the joining of substructures in-situ without the need for additional metallic bolts or ceramic. An homogeneous, and therefore strong, joint can be produced by implementing molten silicon as a joining material which reacts with carbon, either from the joining specimen or introduced as a paste to the joining surfaces, to stoichiometrically form silicon carbide so the joint is as strong and thermally stable as the basis C/C-SiC material.

The typical areas of application for CMC lie where metals, or superalloys, can no longer be taken into consideration due to high thermomechanical loading, and contains all areas of lightweight structures. However, if the application is in an oxidising atmosphere carbon burn-out of both the fibres and the matrix will start at temperatures as low as 450 °C. As a consequence, carbon based CMCs can only be utilised for limited lifetime applications. Even oxidation protective coatings will only reduce material degradation rather than to prevent oxidation completely.

The LSI process and examples of CMC applications are discussed in this paper. Successful applications for the high temperature regime are space reentry structures. Commercially attractive applications within the medium temperature regime take advantage of the excellent tribological properties (e.g. brake disks) of the material. For temperatures below 450 °C (carbon burn-out), CMCs are suitable for expansion sensitive applications due to their near to zero coefficient of expansion.

## Applications of non-oxide CMCs

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**Keywords:** Ceramic Matrix Composites, Fiber-reinforced Ceramic, Body Flaps, Bearings, Ceramic Fibers

Ceramic matrix composites (CMCs) with non-oxide matrices have drawn attention as candidate materials for high temperature applications for many years with the goal to increase system efficiencies through uncooled structural components in power stations and aircraft engines. Silicon carbide (SiC) is the favorite matrix material due to its creep resistance and mastered processes for manufacturing CMCs with this matrix. Heat exchangers, integral turbine blades and disks, combustion liners, filters are examples to which comprehensive studies have been dedicated with preference of silicon carbide fiber reinforced SiC (SiC/SiC) since a superior oxidation resistance over carbon fiber reinforced SiC (C/SiC) was anticipated.

While in ageing tests life times of 10,000 hours and more could be realised without degradation of the CMCs, tests under conditions closer to real applications, i. e. including creep loads and/or gas flows, dramatically increased the speed of degradation reducing life times. Accordingly, programs studying CMCs in turbine combustors, waste incineration plants and heat exchangers have not yet lead to a break through in replacing metallic components. All results have shown that only a limited useful lifetime can be reached under service conditions. The basic drawbacks in all cases have been fiber and interface degradation under the oxidative and corrosive influence of the environment.

All attempts to overcome these drawbacks have not succeeded yet. SiBNC-fibres have shown promising improvements at high temperatures in air, but the transfer into industrial scale manufacturing has failed. Likewise the development of corrosion resistant fibre matrix interfaces has not reached more than lab scale. Furthermore, it has to be taken into account that SiC itself is oxidising and corroding in combustion atmospheres and that chemical equilibrium and diffusion processes become increasingly relevant at higher temperatures and will limit the life times of any material, which – like CMC – relies in its essential properties on structures with micrometer dimensions.

As a consequence, the potential of CMCs can only be utilized in short- time high-temperature applications and at low temperatures, in case an extended lifetime is required.

A favorable CMC application at high temperature is to build structural components for re-entry space vehicles from C/SiC, because full advantage can be taken from its outstanding thermo-mechanical properties during the short exposition to high temperatures. An example with pioneering character is a set of large C/SiC components, with a pair of body flaps being the most challenging one, as the European contribution to the NASA project X-38 using their high temperature strength and their low weight. This is providing an increase of flexibility for mission profiles and capability. A successful flight test will lead to the application in the operational system "Crew Return Vehicle" for the International Space Station.

Successful applications in the low and medium temperature regime are using the reliability and ductility of CMC and favourable tribological properties. CMC components in journal bearings for pumps help to increase their loadability and reliability. Meanwhile, service experience of several years has been achieved confirming the usefulness of this CMC application. Glass handling pads have increased life times compared to C/C components, nozzle flaps in jet engines are – at rather low temperatures – state of the art.

## Failure Behavior of Three Dimensional Hi-Nicalon/Silicon Carbide composites Fabricated by chemical vapor infiltration

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Silicon carbide fiber reinforced silicon carbide composites (SiC/SiC) are the most potential thermal-structure materials to be used in advanced aero-engines, space, and fusion power reactors. Many investigations have been conducted on one dimension (1D) and two-dimension (2D) woven SiC/SiC composite materials. Recently, attention has been focused on three-dimension woven or braided ceramic matrix composite materials in order to meet mechanical and thermal requirements under most complex loads. In the present paper, the authors fabricated three dimensional textile Hi-Nicalon SiC/SiC composites by chemical vapor infiltration and examined the failure and mechanical properties.

The stress-displacement curve of the composites exhibited significantly non-linear failure behavior. As the temperature was increased from room temperature to 1300°C, the flexural strength of the 3D Hi-Nicalon SiC/SiC composites was increased from 920MPa to 1010MPa in vacuum. The failure behavior of the composites changed with increase of the temperature, which was attributed to the interfacial bonding between fiber and matrix. At room temperature, the stress drop was very gradual after the maximum stress point. However, the failure behavior became brittle and the composites exhibited steep stress drops after the maximum stress point at high temperatures. It has been reported that the thermal expansion coefficients of the silicon carbide matrix and the Hi-Nicalon fiber were  $2.2 \times 10^{-6} \text{K}^{-1}$  and  $5.3 \times 10^{-6} \text{K}^{-1}$ , respectively. After the composites were cooled down from the infiltration temperature to room temperature, a tensile stress was generated cross the interfacial layer. As a result, it was easy for the fiber to be pulled out from the silicon carbide matrix. If the temperature was increased above the silicon carbide infiltration temperature (1100°C), a compressive stress was created cross the interfacial layer. Hence, the fiber was very difficult to pull out. The pull-out length at 1300°C was much shorter than at room temperature. For the three dimensional textile SiC/SiC composites, the bundle/bundle interfacial bonding is usually considered as a kind of weak interfacial bonding because of the pores residual in the composites caused by the "bottom neck effect". Accordingly, fiber bundle pullout was always observed at both room temperature and high temperature.

The shear strength of the 3D Hi-Nicalon SiC/SiC composites was measured by the short bending beam method, and the shear failure behavior of the stress-displacement curve was similar to that of bending failure behavior. The obtained value of shear strength was 67.5MPa, which is much higher than that of 3D C/SiC textile composites. Different from two-dimensional CFCCs and the other laminated composites, interlayer debonding was not observed in the present composites. The results indicated that the present 3D Hi-Nicalon SiC/SiC composites exhibited good shear resistant and isotropic properties.

In order to determine the fracture toughness of the composites, samples were notched and tested in a three-point-bending sample. The fracture toughness was  $41.5 \text{MPa}\cdot\text{m}^{1/2}$ , which was ten times of monolithic ceramic materials ( $3.5 \text{MPa}\cdot\text{m}^{1/2}$ ) and two times that of 3D C/SiC composites ( $20.3 \text{MPa}\cdot\text{m}^{1/2}$ ). Microstructure observation revealed that the surface of Hi-Nicalon SiC fiber was much smoother than that of T300 carbon fiber. Consequently, it was very easy for Hi-Nicalon SiC fiber to be pulled out from the SiC matrix, leading to higher fracture toughness. Also, the work of fracture was introduced to represent the toughness of the 3D Hi-Nicalon SiC/SiC textile composite materials. The work of fracture was obtained from the characteristic area under the load-displacement curve divided by the cross section of the specimen. The average work of fracture as high as  $28.1 \text{kJ}\cdot\text{m}^{-2}$ , which is the nearly three times that of 3D C/SiC composites and six times that of laminated SiC ceramic matrix composites ( $4625 \text{J}\cdot\text{m}^{-2}$ ), respectively. Instrumented Charpy impact tests were conducted to determine the dynamic fracture behavior of the composite materials, and the value is  $36 \text{kJ}\cdot\text{m}^{-2}$ . In addition, the composites could also endure the impact penetration by a steel nail without severe fracture. The results indicated that 3D SiC/SiC composite materials exhibited an excellent impact damage tolerance.

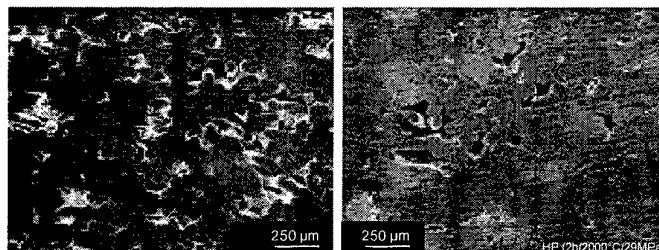
## Microstructure and mechanical properties of CVI-infiltrated C/C-Composites before and after hot pressing treatments

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**Keywords:** C/C-Composites, Hot pressing, Microstructure, Graphitization, mechanical properties

C/C-Composites can be simultaneously graphitized and post densified by thermal/mechanical treatments like hot pressing or hot isostatic pressing. The microstructural changes during these treatments lead to an improvement of the properties of these materials. In this work investigations were carried out in order to study the influence of hot pressing treatments on the microstructure and mechanical properties of CVI-infiltrated carbon fiber felts.

The results of the microstructural investigations confirmed the simultaneous graphitization and densification of the samples after hot pressing. In fact, after these treatments the bulk density of all samples increased while their open porosity decreased. This densification effect can be visualized by means of light (LM) or scanning electron microscopy (SEM) such as in the figure below. The anisotropy of the pyrocarbon matrix, characterized by polarized light microscopy (PLM) and X-ray diffraction (XRD), increased after hot pressing showing the progress of the graphitization mainly in the highly textured (rough laminar, RL) pyrocarbon sheets. In fact, with increasing process parameters (temperature, duration, load) the extinction angle  $A_e$  (PLM) and the apparent layer stack height  $L_c$  (XRD) increased while the interlayer spacing  $d_{002}$  (XRD) decreased.



SEM micrograph of a polished sample showing the densification effect after hot pressing treatment

The results of three-point bending tests carried out on samples before and after hot pressing treatments reveal that the mentioned microstructural changes (densification and graphitization) enhance the mechanical properties of C/C-Composites in terms of increased toughness and flexural strength. The distinct increase of the flexural strength of the samples after hot pressing can be explained by the post densification effect resulting from these treatments. All samples showed a „quasi ductile“ load-deflection curve with a more or less pronounced deviation from linearity zone. After hot pressing this zone becomes distinctly larger showing an increase of the samples toughness. The toughness increase was confirmed with scanning electron microscopy investigations on the fracture surfaces showing more pullout by the hot pressed samples. This toughness increase can be explained by the graphitization progress leading to more and more pronounced sublayers within the highly textured (rough laminar) part of the pyrocarbon matrix where a microdelamination occurs leading to a zigzag fracture surface that was observed using scanning electron microscopy.

## **Fiber reinforced Ceramic matrix composites through CVR**

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Toughening of ceramics through introduction of a second phase in form of particles, flakes, whiskers, fibers etc. has been well established. The interest in so developed ceramic matrix composites is continuously growing due to the great flexibility in designing and tailoring of properties of these multicomponent systems. Fiber reinforced ceramic matrix composites offer higher strength and toughness than any other class of ceramic matrix composites. Though the development of particulate and transformation toughened ceramics and composites have attained more matured status, the fiber reinforced ceramic matrix composites has still to go a long way. Presently a number of techniques are available to process Ceramic matrix composites, predominantly, melt infiltration reaction sintering technique, Chemical Vapour Infiltration, sol-gel, preceramic polymers etc. Each technique offers characteristic advantages and suffers disadvantages. In our laboratory, we have used Chemical Vapour Reaction (CVR) technique to produce ceramic coatings on carbon/carbon composites as well as to develop fiber reinforced ceramic matrix composites. Carbon fibers as well as silicon carbide fibers were used as reinforcement. In one series, base composites were made with resin derived carbon as the base matrix while in second series, silicon oxycarbide matrix composites were made with the same fibers as reinforcement but matrix was derived through sol-gel technique. Silicon and its compounds were used as the gaseous source. Chemical Vapour Infiltration (CVI) was used to convert carbon matrix in Carbon-carbon composites and excess carbon in Silicon Oxycarbide matrix composites to Silicon carbide. The microstructure of the coatings and of the composites has been studied using SEM, XRD etc. The effect of the matrix type, reaction temperature, reacting mixture etc. on the density and structure of the composites has been studied leading to optimization of the reaction conditions. The mechanical properties and fracture behaviour studies on the densified composites showed much improvement in the fracture toughness of the composites. These composites exhibited oxidation protection at 1000°C for quite long time, a many fold advantage over base carbon/carbon composites. Details will be presented.

## **SiC Matrix Composites for High Temperature Applications**

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Keywords: SiC-Matrix, CVR, Low-Cost, C-C Composites

SiC matrix composites offer excellent high temperature properties. However, their commercial applications are hindered by high manufacturing costs as well as lengthy processing. A new process to produce large scale, thick section SiC matrix composites was developed based upon chemical vapor reaction (CVR). Low cost, (below \$100/kg) carbon-carbon composites are manufactured in one manufacturing step. Subsequently, CVR-SiC processing is carried out to achieve three functions 1) CVR-SiC coatings, 2) CVR-SiC matrix, 3) CVR-SiC fibers and CVR-SiC matrix simultaneously. The scalability of this process up to 1m x 1m x 8cm size panels have been demonstrated. Specific applications includes leading edges, turbomachinery parts for reusable launch vehicles as well as fixtures for the semiconducting processing industry. Resulting thermomechanical properties of this new class of SiC composites are on par with conventional CVI-SiC composites. Through-the-thickness thermal conductivity seven to eight times other commercial SiC composites have been achieved. Significant reduction in cost and processing time has been demonstrated, combined with the ability to produce thick parts. Processing and properties details, as well as applications of this new technology will be presented.



## Improving Damage Tolerance of C/SiC

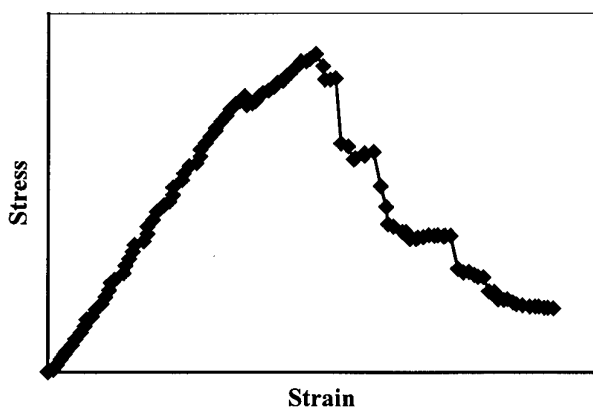
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**Keywords:** C/SiC, inner siliconizing, quasiductile, damage tolerance, bending test

Carbon fiber reinforced silicon carbide (C/SiC) is widely proposed as an advanced material in the field of high temperature applications. This CMC utilizes the advantages of silicon carbide by reducing the main drawback - its brittleness - through fiber-reinforcement. All over the world research focuses on improvements concerning high temperature stability - especially in oxidizing media - and damage tolerance.

As a relatively low-cost method, the liquid silicon infiltration process prevails against the CVI (chemical vapor infiltration) regarding industrial applications. In this process, a porous body of carbon fabric and glassy carbon is built first, then the C/C-material is infiltrated by liquid silicon to transform the matrix into silicon carbide. Ideally, this leads to a dense material of carbon fibers and a silicon carbide matrix with a quasiductile damage behavior. But during the infiltration and reaction step, an attack of carbon fibers by liquid silicon cannot be prevented. A brittle damage behavior in the case of a uniform matrix-conversion is the result.

To improve the mechanical properties, a process which could be described as "inner siliconizing" is used to produce C/SiC. In this case, silicon powder is added at the beginning. A dense body of carbon fibers, phenolic resin and silicon powder is produced in the first step. After carbonization, the phenolic resin is converted into glassy carbon. The close mixture of the matrix components silicon and carbon cause a complete formation of silicon carbide by preservation of the carbon fibers during the last step, the siliconizing. This method necessarily leads to a porous material. The stress-strain-diagram indicates the pseudoductile damage behavior.



Stress-strain-diagram of C/SiC-material produced via "inner siliconizing"

The object of this paper is the processing of C/SiC using "inner siliconizing" and the characterization of this material mainly by microscopy and the bending test.

## SiC/SiC Composites by 2-step Reaction-Bonding Method

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Keywords; SiC/SiC, composites, reaction bonding, melt infiltration

8-harness satin woven SiC fiber fabric (Tyranno, ZMI) reinforced SiC composites were fabricated by 2-step reaction-bonding method. The preform consisting of woven SiC fabric with phenolic resin and nonwoven C fabric with phenolic resin and Si powder was pyrolyzed at 1000°C for 1 h in Ar and impregnated by phenolic resin, then repeated this pyrolysis/impregnation process. After pyrolyzing, this preform was reaction-bonded (1st step, at 1450°C) between carbon from phenolic resin and Si powder formed SiC and pore at nonwoven C fabric. And SiC fabric was covered with amorphous carbon from phenolic resin. After this first reaction-bonding, the porous preform was infiltrated with liquid Si (2nd step, at 1450°C). Liquid Si infiltrated into porous SiC at nonwoven C fabric, however, SiC fabric was protected from liquid Si by amorphous C.

The bulk density and open porosity of the composites were  $\sim 2.2 \text{ g/cm}^3$  and 0.5 %, respectively. Silicon infiltration was seemed to be homogeneous. The flexural behavior was linear elastic up to the first blip at  $\sim 140 \text{ MPa}$ , and showed the small abrupt drop of the stress followed by a nonlinear stress increase to a maximum, followed by continuous stress decreased. This means that the carbon coating from phenolic resin on the SiC fabric protected SiC fabric from the attack of molten silicon. The flexural behavior depended on the ration of Si/C at nonwoven C fabric. The flexural strength and elastic modulus of this composites were 140~250 MPa and 110~160GPa, respectively.

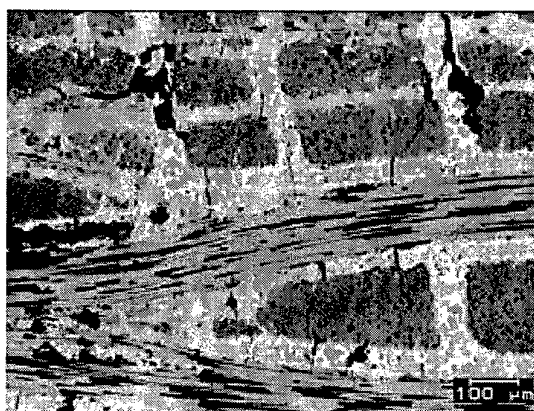
## Influence of Process Parameters on the Thermophysical Properties of C/C-SiC

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**Keywords:** characterisation, LSI-process, graphitization, thermal conductivity, emissivity

Ceramic matrix composites (CMCs) with low porosity in one cycle are obtained via the well established Liquid Silicon Infiltration Process (LSI), being characterized by short processing times and fairly low manufacturing costs. The key step is the infiltration of liquid silicon in porous carbon/carbon composites (C/C) whose distinct microstructure is built in the preceding pyrolysis step of carbon fibre reinforced plastics. Those were produced by resin transfer moulding (RTM) in a first step. This process leads to C/C-SiC composites being characterized by high mass-specific properties in combination with an extreme thermal shock stability. Applying special process parameters the microstructure as well as the physical properties can be tailor-designed to match specific requirements. The properties of C/C-SiC, especially thermophysical properties such as thermal expansion, electrical and thermal conductivity as well as the spectral emissivity, are mainly influenced by the selection of the fibres, while the specific heat capacity is due to both, fibres and matrix properties. The thermal conductivity of C-fibres and thus of a composite is considerably increased with pyrolysis and graphitization temperature as known from C/C-composites.



SEM-micrograph of C/C-SiC specimen derived from graphitized C/C-intermediate.

This paper reports on the influence of various C-fibres and the microstructure, obtained by pre-treating C-fibres, on the thermophysical properties of C/C-SiC. Therefore, C-fabrics were thermally pretreated and submitted to LSI-processing (polymer infiltration via resin transfer moulding, pyrolysis and siliconizing). Another route is to graphitize the C/C intermediate with subsequent siliconizing. The resulting CMCs are characterized by microscopy, and thermophysical methods. Emissivity is measured by means of the radiation comparison technique at temperatures between 800 and 1800 °C, whereas thermal conductivity is obtained by applying the comparative technique in the range 50 to 1000 °C. In addition, thermal conductivity can be calculated from thermal diffusivity, density, and specific heat capacity of the material. The thermal diffusivity is measured by means of a special technique with intensity modulated light beam at temperatures ranging from 300 to 2000 °C.

# REACTION BETWEEN LIQUID ALUMINIUM OR LIQUID SILICON AND COMPOSITE CARBON-CARBON MATERIALS

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**Keywords** : silicon, aluminium, carbon- carbon, infiltration, reactivity, SEM.

## INTRODUCTION

There is a great deal of interest in reaction bonded metal carbide coating on carbon materials. This processing method has the special advantages of combining thermal shock resistance, strength and fracture toughness to carbon / carbon materials, with low abrasive and oxidative wear, and a simple and short production route.

Reaction bonded metal carbide coating on carbon materials were obtained by melt infiltration of aluminium or silicon into porous carbon / carbon preforms. The prepared samples were examined by scanning electron microscopy and X-Ray diffraction. The average thickness of the SiC layer versus time was determined from the electronic micrographs.

## CORROSION OF C/C MATERIALS BY LIQUID ALUMINIUM

The C/C composites dipped into molten aluminium present a heterogeneous corrosion effect due to their 2D structure. The carbon pitch is preferentially attacked by the metal as it surrounds the carbon fibers which exhibit a higher resistance to corrosion. The formation of aluminium carbide from graphite produces a large volume increase (235 %) which induces stress between the carbon layers, causing cracks then rapid delaminating and finally 3D splitting of the sample.

The cleavage is sometimes random due to inhomogeneous impregnation inside the same C/C sheet, as macropores reduce locally the strength of the test-bar by corrosion. After comparing the failure resistance of commercial composites, it is obvious that the use of non-graphitable cokes enhances the mechanical properties linked to the formation of diamond-like C-C bonds instead of graphitic ones. In the same way, heat treatment at high temperature must be avoided as it increases graphitisation.

An increase in temperature up to 1100°C is followed by a large increase in wetting and carburisation kinetic of the samples.

## CORROSION OF C/C MATERIALS BY LIQUID SILICON

The reaction between carbon and liquid silicon begins immediately after melting the silicon, and its infiltration into porous carbon/carbon preforms occurs within only a few seconds. To avoid SiC formation during heating to the determined treatment temperature, an original graphite reactor was built, which allowed the silicon and the carbon samples to be heated to 1600 °C without coming into contact and then the liquid was poured onto the substrate. A thin but continuous cubic silicon carbide layer appeared at the carbon-silicon interface. The layer thickness formed was independent of time and reached approximately 10 µm after a 24 hours reaction time at 1600 °C. Thus, the initial layer formed has a protecting action, preventing the substrate from further corrosion. The SiC formation is volume expansive, causing cracks to appear and, consequently, deeper penetration of liquid silicon into the carbon substrate.

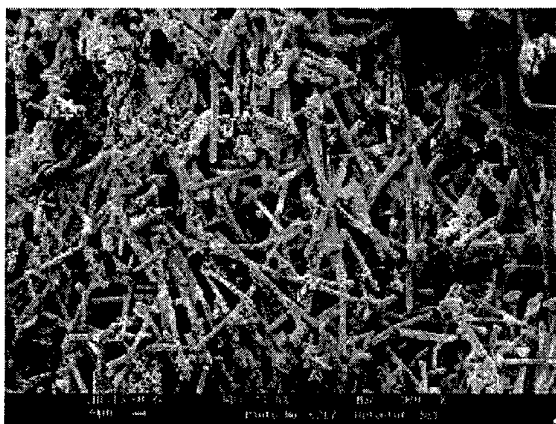
The SiC particles randomly disseminated near the SiC interface in the silicon phase seem to originate from the continuous SiC layer. This continuous SiC layer results from a nucleation and crystalline growth mechanism at the carbon-silicon interface. A local epitaxial growth on the carbon substrate is sometimes observed. The crystal growth induces some strain at the grain boundary, causing part of the layer to disintegrate and some particles to be dispersed in the silicon melt. A solution - precipitation mechanism follows and the thickness of the primary SiC layer remains apparently constant as well as with aluminium carbide layer formation.

## Properties of Porous Si/SiC Fiber Composites Prepared by Infiltrating Carbon Fiber Composites with Liquid Silicon

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**Keywords:** Carbon fiber composites, Silicon carbide, Infiltration, filter, electrical properties

SILCOMP process, a well known method of consolidating Si/SiC composites, utilizes carbon fiber rather than carbon powder as a source of elemental carbon. The SILCOMP process uses carbon fibers in the form of tow, cloth, felt or yarn to build up complex shapes of preform by any of the methods used to make fiber-reinforced polymer matrix composites. During infiltration with molten silicon, the capillary formed by carbon fiber allows rapid infiltration of liquid silicon into the interior of the preform and the individual carbon fibers convert to aggregates of SiC particles by dissolution precipitation mechanism. The resulting Si/SiC materials produced by SILCOMP process are fully dense materials with the SiC content varying 25~90%.



Micrograph of porous Si/SiC fiber composites prepared by infiltrating carbon fiber composites with liquid silicon.

In this study based on infiltration techniques similar to SILCOMP process, electrically conductive porous Si/SiC fiber composites were prepared by partial infiltration of liquid silicon into porous carbon fiber composite preform. The present work is aimed for development of a fabrication route by exploitation of porous carbon fiber composites to yield an electrically heatable porous SiC fiber filter element. The effects on the electrical and mechanical properties of the resultant Si/SiC fiber composite materials were investigated by varying molar ratios of infiltrating liquid silicon and carbon preform, which consequently determined a level of direct contact of the former with the latter.

## Continuous furnace for carbide and nitride ceramics

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Keywords: continuous-, vacuum-, pressure sintering, reaction bonding, silicon carbide, composite material

More often, price requirements are limiting the usage of technical ceramics in industry. Mainly the firing costs for high-volume parts are a problem for economic production. The need of large batch furnaces for cost reduction demands "discontinuous" green part processing and final machining and inspection. Additionally, with increasing size the homogeneity in sintering cannot be guaranteed because parts close to heating elements will get more sintering energy compared to parts somewhere in the middle of the furnace.

Therefore continuously working equipment like tunnel furnaces and roller heart kilns were developed and economically used in a wide field of ceramics. However, up to now these types of furnaces are not available for nonoxide ceramics which require temperatures up to 2400°C and inert, vacuum or gas pressure atmosphere for sintering.

FCT has developed and built a totally new furnace system for continuous sintering up to 2400°C in vacuum and with inert gas up to a pressure of 1 MPa. With this sinter equipment it is possible to produce carbide, nitride ceramics and composite material with high flexibility.

With this new sintering approach, the production of different type of high performance ceramics and composite materials can be optimised by improved heat treatment in a more homogeneous temperature field and reduce sinter costs due to a high capacity of a relatively small furnace. Sintering as well as reaction bonding for silicon carbide and carbon based materials is possible with this type of new furnace.

Temperatures up to 2400°C and a pressure in between  $10^{-3}$  and 1 MPa can be realized. The useable cross section is W 260 x H 160. Length of heating zone is 3600 mm allowing heating rates of 100-300 k/h and a capacity of 1 m<sup>3</sup>/day. Technical details for operation and initial results with this furnace are presented.

## Development of SiC/SiC Composites from Si-based Polymer Blend by Radiation Application

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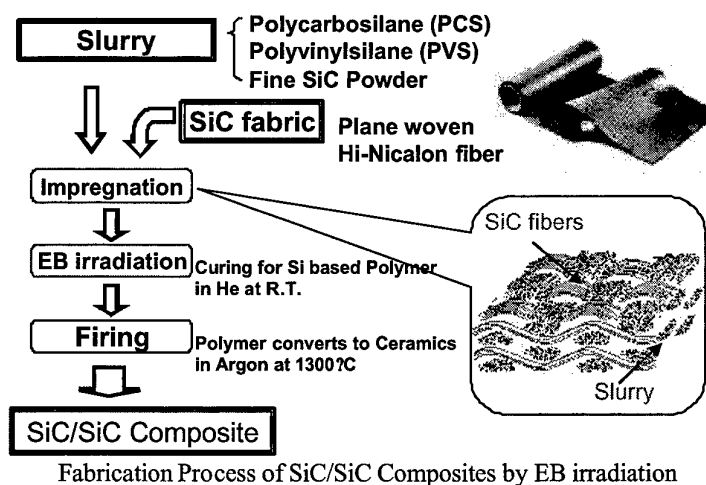
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**Keywords:** Electron Beam Curing, PIP, Polycarbosilane, Polyvinylsilane,

The ceramic matrix composites (CMC) with high strength and heat-resistance are strongly required for the advanced technologies such as nuclear fusion reactors and space planes. Silicon carbide (SiC) fiber has high potentiality for the fiber reinforcement. We had succeeded to improve the heat resistance of the fiber by decreasing the oxygen content, using electron beam (EB) irradiation in the curing process. The processing of silicon carbide (SiC) fiber reinforced SiC composite has been studied in the recent two decades and several manufacturing processes were developed. Polymer impregnation and pyrolysis process (PIP) has been well studied, but the process needs to repeat the impregnation by several times. In our process, EB irradiation was applied for the curing of the impregnated polymer as matrix. Also, new polymer such as polyvinylsilane (PVS) was incorporated into the precursor polymer (PCS).

The fabrication process of SiC/SiC composites is shown in figure. Polycarbosilane (PCS) and PVS are dissolved in benzene and impregnated into two-dimensionally woven SiC fabric. After impregnation, the material was heated up to melting point of the blend polymer, and formed to a shape of sheet by press machine. The pre-ceramic composite was irradiated up to 15 MGy by 2 MeV-EB in helium at ambient temperature for curing of polymers in the composite, and then fired at 1373K in argon.



By applying EB curing technique, the shape and the size of the composite do not change even after firing. The fracture behavior of the CMC was improved by the application of new silicon polymer such as PVS. The composite showed a ductile property and we could make the composites with fiber volume fraction over 50-vol%.

## **Fabrication of Fiber Reinforced Si-B-C-N Composites by the Polymer Precursor Method**

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Keywords : FRC, PIP, Si-B-C-N, infiltration, mechanical, properties

FRCs (fiber reinforced composites) using an Si-B-C-N matrix was fabricated by the PIP (polymer infiltration and pyrolysis) technique. A mixture of tris(hydridosilylethyl)boranes and oligovinylsilazane (ceramic yield : 82%) was used for the infiltration. The precursor showed fair infiltration behavior even if it was not diluted with solvent due to its low viscosity at room temperature. Homogeneous distribution of the Si-B-C-N matrix was observed in- and outside the samples even after the first infiltration and pyrolysis process. The effects of processing conditions during infiltration, crosslinking and pyrolysis on the microstructure and properties of the composite were investigated, and the decrease of porosity with increasing the number of infiltration and pyrolysis cycles was observed to minimize the required number of infiltrations. First results on the mechanical properties are reported.



## Oxidation behaviour and mechanical properties of carbon fibre composites with methylphenylsiloxane - based matrix and pyrolytic carbon coating

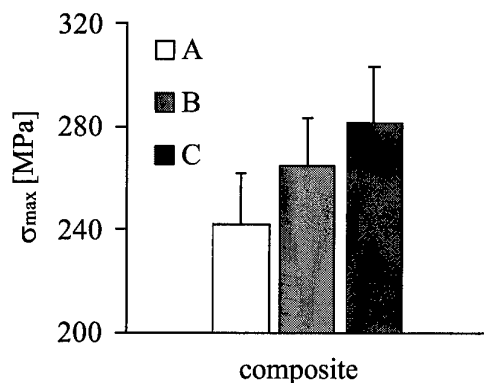
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**Keywords:** carbon fibre, methylphenylsiloxane, composite, pyrolytic carbon, oxidation, mechanical properties

Carbon fibre reinforced carbon matrix composites, which are - thanks to excellent mechanical properties of carbon fibres at ultimate temperatures - potential candidates for high temperature structural applications, suffer from proneness to oxidation. For medium conditions of application (up to 600 - 700°C in air), utilisation of silicon containing, oxidation resistant matrix is promising. In the present study, properties of carbon fibre composites with a matrix derived from poly-methylphenylsiloxane-based resin were investigated. During pyrolysis at 600 -1000°C in nitrogen the resin is converted to glassy material (so called black glass) stable in air roughly up to the temperature of its pyrolysis. At RT the viscosity of the resin is suitable for wet winding process. Unidirectional composites with Toray M46 fibres were cured at 225°C, twice impregnated and pyrolysed at 1000°C in nitrogen. After oxidation in dry air at 600°C for 1 h the detected weight loss of  $\approx 3-4\%$  was accompanied by releasing of fibres from the surface. Therefore, the specimen surface was stabilised by depositing a pyrolytic carbon layer (CVI/CVD from propane in tumbling bed, thickness 3-5  $\mu\text{m}$  or 9-11  $\mu\text{m}$  after 12 hrs or 24 hrs of deposition, respectively). Under oxidation conditions above the layers were effective in reducing the weight loss to  $\approx 1\%$  and increasing the bending strength measured in vacuum at 600°C (see Figure).



Bending strengths at 600°C of uncoated composite (A) and composites coated with pyrolytic carbon (B - 12 hrs, C - 24 hrs) after 1 hr oxidation in air.

Under bending load the specimens failed by a series of delaminations. By evaluation of J-integral the overall energy needed to break the specimens turned out to increase with the coating thickness. Dynamic elastic and shear moduli measurement by a resonant beam technique at RT revealed that the oxidation treatment resulted primarily in a drop of the shear modulus (by up to 16 - 20 %) while the elastic modulus remained almost unchanged.

## **C fibre reinforced ceramic matrix composites manufacturing by a combination of CVI, PIP and RB.**

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**Keywords:** Continuous fibre composite, Chemical Vapour Infiltration (CVI), Polymer Impregnation and Pyrolysis (PIP), Reaction Bonding (RB).

Continuous carbon fibre SiC matrix composites were prepared by combining Chemical Vapour Infiltration (CVI), Polymer Impregnation and Pyrolysis (PIP) and Reaction Bonding (RB). 2D carbon fibre cloths were stacked and coated by CVI with C and SiC thin layers. They were subsequently infiltrated with carbon precursor resin, pyrolysed in inert atmosphere and reacted with molten silicon. The infiltration and pyrolysis step was repeated until a satisfactory carbon content was reached. The process parameters were correlated with the final micro and macrostructural properties. It was found that the preliminary CVI coating was essential to ensure a non brittle behaviour to the composite: C layer tailors the fibre/matrix adhesion allowing crack deflection along fibre axis and fibre pull-out; SiC layer protects carbon fibres from reacting with molten silicon and degrading their mechanical properties. The conversion of C, obtained from resin pyrolysis, into SiC was found dependent on carbon structure and reaction time: full conversion of C into SiC could not be obtained when the carbon particles, originated from resin pyrolysis, exceeded a critical size. Different approaches were investigated to control carbon structure and tailor carbon porosity: SiC powders addition (directly in the resin or during a preliminary step) and further process modifications led to significant improvements. Mechanical performance were evaluated by flexural strength tests. Maximum modulus of rupture obtained up to now is 310 MPa corresponding to 1% strain to failure; generally about 150 MPa residual strength is observed at 1.5% strain.

## **C/SiC-C composite production by resin pyrolysis-reaction bonding-CVI joint process**

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**Keywords:** C/SiC-C composite, pyrolysis, reaction bonding, CVI, Si-powders.

One of the main drawbacks affecting CMC and limiting their spreading is high cost. Effective chances to make CMC products cheaply available to any application are hindered by production cycles still too expensive and long lasting. In this paper a fabrication route is examined aiming to take advantage of different processing techniques, through their concurrent work.

The starting material is a Carbon/Carbon preform consisting a 2-D woven fabric laminate plate, which is given the necessary coherence by a partial Chemical Vapour Infiltration treatment. By means of this initial treatment, a thick (a few micrometers) layer of pyrocarbon is deposited onto fibre surface, to serve both as a toughening interphase for the final material and as an agent to possibly prevent fibres from chemical degradation: layer thickness is established according to these aims. The following step takes place with fibre impregnation by a ceramic precursor thermosetting polymer (phenolic type) carrying a large percentage of metal Silicon powders.

Final step of the process is resin pyrolysis, carried out in a carbonising atmosphere ( $\text{CH}_4$ ). Effects sought by driving this treatment are of two kinds. The first one is a chemical reaction occurring between Si-powders and resin pyrolysis-yielded carbon, to produce a SiC phase in the matrix. At the same time, pyrocarbon coming from Methane molecule dissociation is committed with filling up voids left in the matrix during the pyrolysis/reaction process; as a result, final matrix structure production is completed by formation of a second phase, purely consisting of pyrocarbon.

The product of the whole process is a C/SiC-C composite being characterised by a low cost deriving from a short lasting fabrication route. Overall process duration is kept short by achieving complete densification of the sample plate without driving any single step more than one time. Such a straight-route process is intended to yield a suitably strong and tough material to be implied in many HT-applications, even if wide adjustment of all process parameters is needed to reach optimum configuration, and therefore obtain the highest possible material quality.

## Preparation of AlN Whiskers and Application to Composite Materials

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Keywords: AlN powder, AlN whisker, Floating-type direct-nitridation, Composite materials

Aluminum nitride (AlN), which is characterized high thermal conductivity and excellent electrical insulation, is a remarkable material for substrates and packages. The authors have studied a continuous production process of high-purity AlN powder by a direct nitridation process, and have reported that AlN whiskers deposited on the reactor wall. The properties of the whiskers are expected to have high thermal conductivity and strength. It was reported that the AlN whiskers grew by vapor-liquid-solid (VLS), as Fe droplets were observed at the top of the whiskers. Whisker property requirements for filler applications are much different from those for substrate and packaging applications. It appears that whiskers comprised of high purity and of high stability are desirable for filler applications. In this study, the pure whiskers were synthesized by floating-type direct-nitridation of aluminum (Al) powder, and also the application to composite materials were investigated.

An atomized ultrapure Al powder was used as a raw material in this experiment. The purity was 99.99% and the mean particle size was around  $15\mu\text{m}$ . The amounts of metallic impurities and oxygen are listed in table 1. The nitrogen and ammonia having 99.9995% were supplied into a reactor. An alumina tube of 1000mm long with 42mm in inner diameter was vertically placed as the nitridation reactor. At the bottom of the reactor a feeder filled with about 120g of ultrapure Al powder was installed. The Al powder as a raw material was fed into nitrogen stream from the bottom of the reactor. Ammonia gas was also introduced into the reactor through another feeding tube with 5mm in inner diameter. Nitridation was carried out in a nitrogen and/or gas mixture of nitrogen and ammonia at 1350 to 1550° for 10 to 80 min. AlN ceramics were obtained by pressureless sintering at 1900° for 120 min and by hot-pressing at 1900° for 120 min under 30MPa.

Table.1 Metallic impurities and oxygen content in Al powder.

Mean particle size : $15\mu\text{m}$						$\text{O}_2$ content : 0.05wt%							
Metallic impurities	Si	Fe	Cu	Mn	Mg	Cv	Zn	Ti	Zr	B	Ni	V	Ga
Contents [ppm]	2	2	1	<1	2	<1	1	<1	<1	2	<2	<2	<2

Pure white whiskers were deposited on the reactor wall by using nitrogen as a reactant gas. Transparent AlN whiskers, however, were deposited on the reactor wall and feeding tube by using ammonia as a reactant gas. And also a powder mixture of hollow spherical AlN and fine AlN particles were produced. Since the system in this study includes no Fe, the growth mechanism is thought to be proceeded through vapor-solid process (VS). Transparent and high strength AlN ceramics were obtained from the white whiskers by hot-pressing at 1900° for 120 min under 30MPa, however, it could not be obtained from the transparent whiskers. These AlN powder obtained had good sinterability, and high thermal conductive and strength AlN whisker-reinforced ceramics could be obtained through sintering  $\text{Y}_2\text{O}_3$ .

## Room and High Temperature Mechanical Properties of Hot-pressed SiC Chopped Fiber Reinforced SiC Composite

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Keywords: SiC/SiC composite, Hot pressing, Mechanical property, Chopped fiber

Ceramic matrix composites (CMCs) have shown great promise regarding their use as high temperature structural materials. Non-brittle failure properties of CMCs are generally greatest for those that employ continuous fiber in a matrix produced using polymer pyrolysis or chemical vapor infiltration techniques. The main disadvantages of continuous fiber CMCs are their high cost and long manufacturing times. One method to overcome these disadvantages is through use of a sintering densification process and chopped fibers.

The present work is to investigate the effect of processing parameters on the mechanical properties of SiC/SiC composite using BN-coated Hi-Nicalon chopped fibers fabricated by hot pressing. A similar composite using SiC whisker as the reinforcement was prepared using a standard sintering route as a comparison.

An  $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3\text{-CaO}$  system was chosen for fabrication of the SiC chopped fiber reinforced SiC composites as sintering additives, because of their low densification temperature. The volume fraction of SiC chopped fiber with an average length of 1 mm was about 10 and 20 vol%, respectively. The green sheet was prepared using a laboratory scale doctor-blade equipment. The stacked green body was hot-pressed at 1650-1750°C in Ar under a pressure of 40MPa for 1h.

Most of all SiC chopped fibers of green sheets were oriented in tape casting direction and the bulk density of the composites were relatively high. The Mechanical properties were measured at room and high temperatures. The fracture surfaces of the samples were observed by scanning electron microscopy (SEM), and the phases in the samples were identified by X-ray diffractometry (XRD).

## Mechanical and Thermal Properties of Hot-Pressed SiC/SiC Composite Using SiC Matrix Containing Large SiC Grains

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Keywords : SiC/SiC composite, Large SiC grains, Hot-pressing, Thermal and mechanical properties

Continuous SiC fiber-reinforced SiC (SiC/SiC) composites are one of the most attractive materials for high-temperature structural applications. Present authors have studied a fabrication process of SiC/SiC composite using hot-pressing. Green sheets of SiC with  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$ -CaO sintering additives prepared by doctor-blade method and polycarbosilane-impregnated 2D woven Hi-Nicalon cloths with BN-coating were stacked alternately, and followed by hot-pressing at 1650-1750 °C. The composites showed a relative density of 93-94 % and a bending strength of 150-240 MPa. The thermal conductivity was 7-14 W/mK at room temperature, and was nearly the same or slightly higher than that of the composites fabricated by CVI and PIP methods. One of the effective ways to improve the thermal conductivity of SiC/SiC composite would be considered to increase the thermal conductivity of the SiC matrix. In this study, we tried to improve the thermal conductivity of the SiC matrix by the addition of large SiC grains, and room temperature mechanical and thermal properties of the SiC/SiC composite using this matrix were investigated.

An  $\text{Al}_2\text{O}_3$ - $\text{Y}_2\text{O}_3$ -CaO system were used as sintering additives for the  $\beta$ - (average particle size 0.28  $\mu\text{m}$ ) or  $\alpha$ -SiC (average particle size 0.40  $\mu\text{m}$ ) matrix containing large SiC grains with an average particle size of 2-3  $\mu\text{m}$ . Using this matrix, 2D SiC fiber-reinforced SiC matrix composite was fabricated by hot-pressing at 1650-1750 °C for 1h under a pressure of 40 MPa.

Relative density of large SiC grains-added monolithic SiC hot-pressed at 1750 °C was about 96%, and the addition of large grains did not inhibit the sinterability of monolithic SiC. The addition of large grains did not induce the decrease in bending strength at room temperature. Thermal conductivity of monolithic  $\beta$ -SiC increased from 30 to 40 W/mK by the addition of large grains. Furthermore, monolithic  $\alpha$ -SiC with large grains showed a thermal conductivity of 60 W/mK. From these results, the addition of large grains to the  $\alpha$ -SiC matrix would be expected to increase thermal conductivity of SiC/SiC composite without decrease in bending strength. The mechanical and thermal properties of SiC/SiC composite will be presented at the conference.

## **Reaction Bonded Silicon Nitride (RBSN) Reinforced by Short SiC Fibres**

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Swiss Federal Laboratories for Materials Testing and Research (EMPA), Switzerland

**Keywords:** Short Fibre, Processing, CMC, RBSN, Polymer Precursor, Fibre Damage

In the last two decades an increasing interest and intensive research in the field of high performance engineering ceramics, in particular on SiC and  $\text{Si}_3\text{N}_4$ , was observed due to their outstanding properties like high temperature strength, abrasion and corrosion resistance. These properties are interesting for applications in hot parts of machines and systems where corrosive atmospheres, abrasive conditions and cyclic temperature loading is applied (i.e. turbines, heating chambers, evaporator coils). Introduction of ceramic components aims towards an improved long term stability of the systems. The possibility to increase waste gas temperature these systems improves the economic efficiency. Due to the brittle mechanical behaviour these ceramics have to be adapted to the demands of the mentioned engineering applications, meaning a ductilisation by introduction of fibres. Long fibre reinforced ceramics are already used successfully for one decade, but due to their extensive costs, caused by manual labour of filament winding technique they are only applied in cost tolerant branches as air and aerospace applications. To open the advantages of fibre reinforced ceramics to a broader field of applicants as automotive and engineering industry, efforts were made to lower the production cost by means of short fibre reinforced ceramics where mass production techniques as plastic forming followed by a ceramisation via liquid silicon infiltration (LSI) are applied.

Here a new approach of short fibre reinforced ceramic matrix composites (CMC) by mixing of fibres, ceramic and plastification system in a kneader followed by a forming step via pressing is presented. Preforms were achieved by pressing, afterwards debindered and nitrided to form a RBSN (reaction bonded silicon nitride) matrix. Due to the volume expansive character of the nitridation process, porosity of the CMC is lowered during nitridation process. Nitridation is described in terms of Young's modulus, phase composition and development as well as dilatometer behaviour.

Carefully adjusting of nitridation parameters during processing minimises fibre damage. This feature is in particular important for non oxide fibres like SiC which can not maintain their mechanical properties at temperatures above 1400°C.

Compared to LSI-route the lower nitridation temperatures of the alternative RBSN-route prevents extensive fibre damage. This opens the opportunity to use oxidation resistant ceramic fibres instead of carbon fibres which are normally seriously damaged by high temperature processes like LSI.

## Preparation of liquid-phase sintered multilayer composites of SiC – AlN

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Max-Planck-Institut für Metallforschung / Institut für Nichtmetallische Anorganische Materialien  
der Universität Stuttgart  
Stuttgart, Germany

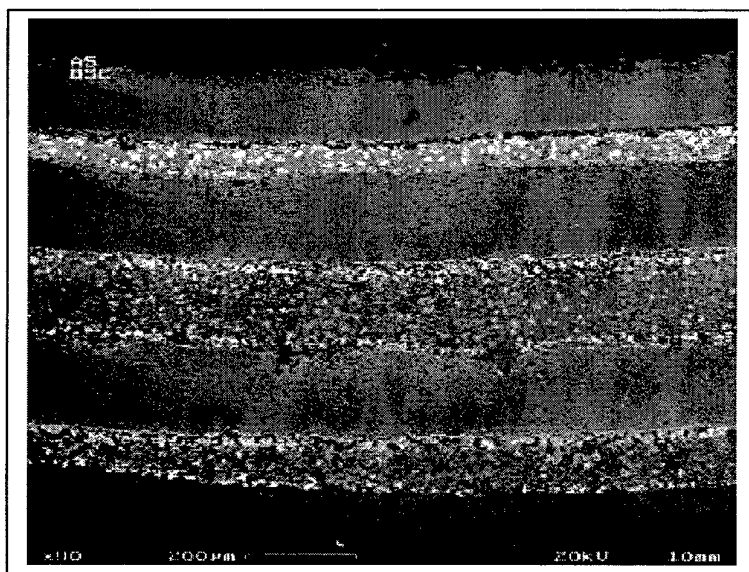
**Keywords:** centrifugal deposition, electrophoretic deposition, liquid-phase sintering, AlN, SiC

The application of functional ceramic materials generally gives rise to substantial mechanical stresses. In the present work, composites of SiC and AlN are investigated in order to combine the good thermal and (fracture) mechanical properties of the two materials.

A multilayer system is chosen since the preparation of two-phase particle composites has been reported to be problematic due to the complete solid solution range between SiC and AlN. However, using AlN-powder and SiC-whiskers, reinforced composites with stable and discrete phases have been described.

The preparation of the composites is based on a wet processing route - aqueous as well as non-aqueous. In particular, sequential centrifuging and electrophoretic deposition are used as shaping methods requiring short-range repulsive forces in the first case and long-range surface potentials in the latter. For liquid-phase sintering, AlN and  $Y_2O_3$  are chosen as additive system for SiC; the commonly used additive for AlN is  $Y_2O_3$ . Applying these compositions means that one has to take measures to prevent the hydrolysis of aluminium nitride in water-based slurries.

Following these requirements, suitable SiC- and AlN-slurries were developed and deposited. After drying and binder burn-out, the samples were liquid-phase sintered under a moderate nitrogen overpressure. Varying sintering conditions were applied in an effort to reconcile the different sintering behaviour of the two materials.



SiC – AlN multilayer composite sintered at 1900 °C and 2 bar nitrogen

AlN starts to densify at lower temperatures and sinters more rapidly than SiC which poses the problem of achieving high densification with as little inter-diffusion as possible.



## **Biomorphic SiSiC ceramic composites from wood fibers**

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**Keywords:** Biomorphic ceramic, wood fibers, SiSiC ceramic

Preprocessed wood fibers are low cost and regenerating materials offering a great potential for ceramic processing. A large variety of different shapes and sizes of wood fibers can be extracted from coniferous and deciduous wood as well as from monocotyledons (e.g. bamboo).

Different wood fiber materials were pressed into circular sheets with a diameter of 150 mm and a thickness of 10 mm. Lignin, a native wood biopolymer, was used as lubricant and binder. The pressed samples were dried and subsequently carbonized at 800°C in inert atmosphere. A weight loss of 75-85 % and a linear shrinkage of 20-45 % occurred. The porous carbon preforms were infiltrated with liquid silicon at 1550°C to form SiSiC ceramic composites.

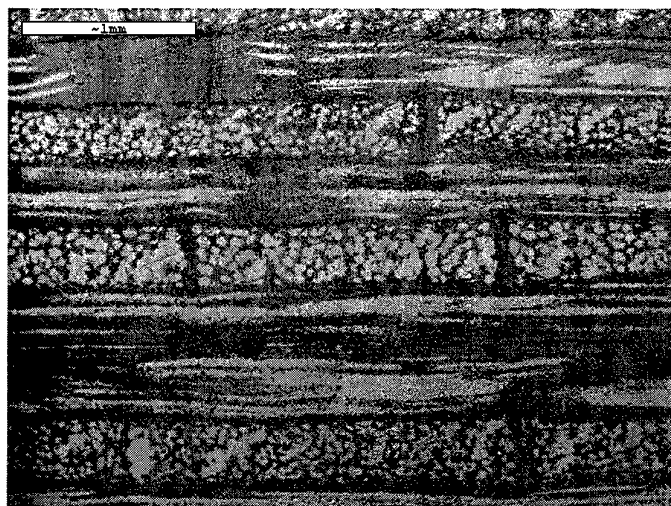
Depending on the fiber to binder ratio, the fiber morphology and the fiber texture the mechanical properties can be tailored in a wide range. The biological aspect of using biomorphous preforms for manufacturing of wear resistant SiSiC ceramics will be discussed.

## Microstructure and Properties of Biomorphic SiSiC Ceramics derived from Pyrolysed Wooden Templates

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**Keywords:** biomorphic SiSiC ceramics, pressing, carbon templates, siliconization, characterisation

The processing of ceramics derived from cellulose containing preforms offers a potential to obtain a new class of material by imitating the biological structure. However, natural products have a high anisotropy due to the non-uniform growing conditions. To overcome this problem, the variation of wooden raw materials and binding agents in combination with the pressing parameters can lead to technical wood blanks with adapted microstructures. In order to get a dense biomorphic SiSiC ceramic the moulding is followed by a temperature treatment (pyrolysis) and final infiltration with pure silicon melt.



Microstructure of a biomorphic, multilayer SiSiC ceramic with stacking sequence 0/90° derived from beech veneers. Composition of the composite: Silicon (white), SiC (grey), Carbon (black). SEM micrograph of a cross section: magn. 35x.

In our studies we used blanks composed of veneers, splints, fibres and C-precursors, respectively. The green-bodies (100 x 110 x 20 mm<sup>3</sup>) were manufactured by using uniaxial pressing technique. Due to the variation of structural and pressing parameters different templates could be obtained which were compared with commercial wooden products. After pyrolysis all templates showed a suitable porosity for the final infiltration with silicon. The structure, elemental composition and mechanical properties of the biomorphic ceramics have been investigated. The texture and microstructure were examined with light microscopy and SEM. By using the Archimedes method the density and open porosity was determined after each process step. The bending strength and fracture behaviour, carried out by the three-point short bending test, was correlated with the structure as well as the composition and distribution of the elements.

## Wood Derived SiC Ceramics with Oriented Porous Structures via Carbothermal Reduction

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**Keywords:** Biotemplating, Carbothermal Reduction, SiC, Filter, Porous Material

In the last decade a growing interest in converting biological structures like paper and fibre-like morphologies (rice husks and flax) into ceramic materials has been reported. A particular field of interest is to reproduce the structure of natural wood into the ceramic state.

Due to the highly anisotropic cellular appearance which cannot be copied by artificial means, ceramic materials converted from wood could be attractive for applications like filters, catalysts, membranes etc. To transform the wood structures into a ceramic it is a prerequisite to convert the wood into a carbon template followed by a ceramisation step. The ceramisation can be carried out by various approaches, whereby the most common method is the liquid silicon infiltration of the carbon template and consequently the reaction to SiC. Hereby the free silicon limits the application temperature and reduces the open porosity by blocking the pores.

This can be prevented by a gas phase infiltration of the pyrolysed woods via evaporation and convection of silicon or gaseous SiO, which can be generated from C/SiO<sub>2</sub> or Si/SiO<sub>2</sub> powder mixtures. SiC is formed due to a high temperature reaction between carbon from the template and the silicon-donating source. As a result porous SiC ceramic is formed.

This work describes the production of porous ceramic structures derived from wood by a new approach via the liquid infiltration of the carbon template with different SiO<sub>2</sub> precursors which initialise a carbothermal reaction in the carbon template at processing temperature. The production route from the wood to the pyrolysed state and the following ceramisation step will be described. Properties of the achieved porous ceramics are examined by different methods and set into correlation to preparation and experimental procedures.

# **Non-Oxide CMCs: characterization/simulation**

**Wednesday, October 3<sup>rd</sup>**

**Morning session**

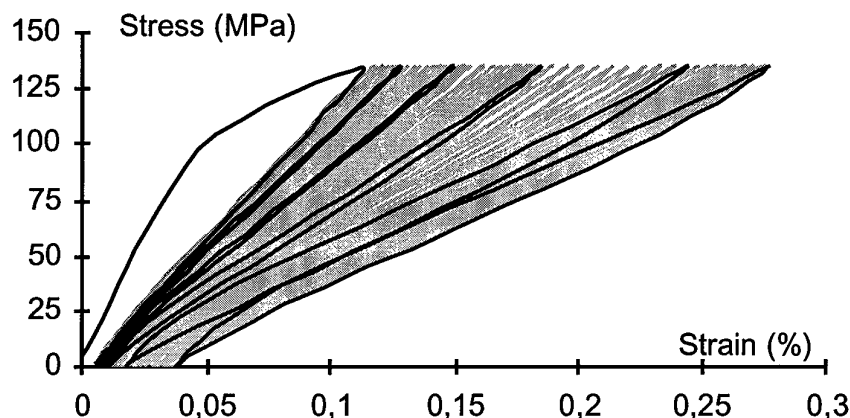
## Anelastic behaviour of ceramic matrix composites during cyclic fatigue

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**Keywords:** mechanical behaviour, anelasticity, internal friction, interfaces, cyclic fatigue

A given material exhibits anelastic behaviour when some internal friction mechanisms are operating. This leads to damping: a certain amount of the strain energy involved during the cyclic load is dissipated into heat. The damping is expressed as the specific damping capacity (SDC) defined by the ratio of the energy dissipated during a stress cycle over the maximum strain energy exchanged per unit volume during that cycle.

In composites reinforced with fibres, several causes of damping are to be considered. There is damping in the constituents themselves, coming from dislocation slip in metal matrix or molecular relaxation in polymer matrix composites. In ceramic matrix composites, the intrinsic damping of fibres and matrix is negligible as regards to the damping due to the frictional shear displacement at the interfaces. Internal friction can be used here as damage indicator. The cracks filled with more or less viscous glass in self-healing non-oxide composites can also be sources of damping.



Typical stress-strain loops recorded during tension-tension cyclic fatigue in SiC/SiC composites.

The aim of the present lecture is to give an overview about the role of material and testing parameters on the damping characteristics of brittle matrix composites. The analysis of anelastic behaviour gives additional information to those obtained from stiffness and residual strain changes.

The main cause of damping during fatigue is the frictional seesaw slip at the interfaces near the matrix cracks. As shown in the above figure, the loop area, and the SDC, increase as fatigue cycling proceeds. That evolution is connected with non-saturated matrix cracking and interface degradation. Conversely, an increase in SDC is observed in saturated cracking situation. The damping depends on the temperature because of residual stresses induced by thermal misfit between fibres and matrix. Another effect is linked with interface modifications occurring at high temperature like oxidation and glass formation. For a given damage level, the changes in damping as a function of cycling amplitude gives some information about details of the stress transfer profile at the bridge. All these features will be described and discussed.

## **Carbon Fibre Reinforced CMCs: Manufacture, Properties, Oxidation Protection**

R. Weiss, Schunk Kohlenstofftechnik GmbH, Heuchelheim, Germany

**Keywords:** In-situ process control, silicon treatments, CMCs, felt reinforcements, CVI/CVD-processes, oxidation protecting coatings

Carbon/carbon composites (C/C) and carbon/carbon silicon carbides (C/C-SiC) are part of ceramic matrix composites (CMC). However, it is an own family of materials which can be modified by the reinforcing materials, the matrix precursors as well as by the manufacturing process.

The large variety of carbon fibre reinforced CMCs applied in industry will be presented from the viewpoint of tailored developments, covering the above mentioned influencing parameters.

The paper presents new developments of C/C-SiC materials for tribological applications in industry as well as for automotive brake systems.

Newest manufacturing and development techniques for in-situ process control for CVI/CVD based CMCs will be shown. In-situ spectroscopic measurements were used for the development of "Rapid CVI impregnations" as well as for new oxidation protecting coatings. This new technique allows process optimizations and scaling up steps within some few experiments and contributes thereby to a tremendous cost and time reduction for new developments.

The combination of CVI and resin impregnation for the densification of CMC enables a decrease in cost and time for larger structural components. Some examples of new applications will be given during the Conference.

A future option for further material modifications are biomaterials as reinforcements which can be converted to carbon/carbon as well as to monolithic ceramics or intermediate material combinations. These new raw materials possess a typical microstructure formed by the nature which can be used in so called biomimetic materials. The activities of Schunk in this new development field will be shown.

The development of new textile preforms offers the opportunity to realise complex structural components without any additional joining and final machining of the parts. As a typical part, a grid carrier system for heat treatments of metal parts (hardening or sintering) was developed at Schunk. The textile preform is made by fibre tow placement (FTP) and densified via the resin impregnation route. The properties of these C/C grids will be discussed with respect to mechanically joined grids.

One of the main limitations of C/C-SiC and C/C materials is the oxidation resistance. The state of the art in oxidation protected CMCs of Schunk will be presented. Development activities are multilayer systems including glass sealing layers based on painting, dipping, and/or Sol-Gel techniques.

The properties of a newly developed self-healing systems, *BoraSiC*<sup>®</sup>, will be presented.

## **Ultrasounds : an essential tool for studying the mechanical behaviour of CMCs.**

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Keywords : stiffness measurement, strain partition, interfacial sliding stress.

The aim of this paper is to show how the use of ultrasounds can be a useful method for studying the mechanical behaviour of ceramic matrix composites.

The non-linear behaviour of CMCs mainly originates from the combination of two damage mechanisms : matrix microcracking and fibre-matrix debonding. Matrix microcracking induces a loss of stiffness. Mode II cracking leads to the opening of the transverse cracks, and therefore inelastic strains, due to fibre-matrix sliding with friction. The loss of stiffness is usually measured using the slopes of unloading-reloading cycles but the choice of the origin of a hysteresis tangent is a particularly hazardous task when some closing-opening effects on the microcracks change the slopes of the hysteresis. Moreover, the inelastic strains in CMCs are the macroscopic indication of the transverse crack opening displacement due to interfacial fibre-matrix sliding. This sliding is subordinate to the direction of the load and thus partly reversible. Therefore, the strain measured when the specimen is completely unloaded only represents the permanent part of the inelastic strain. Consequently, the usual identification underestimates the inelastic strains and overestimates the elastic modulus drop because the reversible part of the inelastic strains can not be separated from the elastic strain. To separate and to identify the two damage mechanisms responsible for the non-linear behaviour of CMCs, it is necessary to perform a strain partition under load.

Ultrasonic characterisation through the complete determination of the stiffness tensor during a test detects all the damage mechanisms. When an extensometer measures the total strain simultaneously with the ultrasonic evaluation, the contribution of the damage mechanisms to the non linear behaviour can be evaluated and a strain partition under load performed. Because wave speed measurements give access to the value of every elastic constants of the material, it is possible to know which coefficients are affected during the damage process and to know the elastic part of the material behaviour only. The formulation and identification of 3D constitutive laws for ceramic matrix composites is then simplified and more accurate. Moreover, this method can give physical explanations for the observed experimental phenomenology and provides a macroscopic method for measuring a key parameter in the behaviour of CMCs : the interfacial sliding stress.

The results of the use of this methodology will be illustrated on various CMCs : 1D and 2D SiC-SiCs, 2D C-SiC and 3D C/C.

## **Fracture Toughness of Thermally Shocked SiC-fibre Reinforced Glass Matrix Composite**

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In ceramic and glass matrix composites reinforced by brittle fibres, elastic fibre bridging and fibre pull-out mainly cause the toughening. Both bridging mechanisms grow in some extent behind the crack tip along the process zone wake. The crack growth resistance increases as the crack propagates and leaves the wake. It is therefore difficult to determine the intrinsic fracture toughness as a material parameter.

The fracture properties of a commercial available SiC-fibre reinforced glass matrix composite were investigated in this study by several techniques. The behaviour of the material after thermal shock loading was compared with the behaviour in the "as-received" condition and after thermal ageing in oxidising atmosphere. The room-temperature properties have been evaluated by using four-point flexure strength and three-point flexure chevron notch techniques. Specimens with straight sharp notch tested in three-point bending were also tested.

The fracture toughness values determined by the chevron-notch tests were affected by the thermal shock and thermal aging conditions. For most thermal shock loadings comparable loss of flexure strength and stiffness of the samples was detected, which has been ascribed to microstructure changes occurred in the glass matrix and in the interfaces during thermal loading. On the basis of the experimental results, the possible mechanisms of damage development under thermal shock conditions in brittle matrix composites were evaluated.

The results also showed that the straight-notch test was unsuccessful to deliver reliable fracture toughness values in the present composites.



## High Temperature Fracture Toughness of a C/SiC (CVD) Composite as used for Screw Joints in Re-Entry Vehicles

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Universität Bremen, Germany

Keywords: Fracture Mechanics, Crack Bridging, Life time prediction, CMC screws

The most prominent feature of CMCs in comparison to monolithic ceramics is their very high fracture energy and toughness due to crack bridging effects. Stress concentrations, e.g. at notches or holes, are reduced by stress redistribution and inelastic deformation. It has been shown that the reinforcing capabilities of various CMC types can be distinguished and assessed by using fracture mechanical test methods like single edge notch beam (SENB) and compact tension (CT). From evaluating the load-displacement behavior under different test conditions and normalizing the maximum load, intrinsic properties like fibre strength distribution or energy dissipation during debonding and pullout can be quantitatively derived.

The material which is investigated here is produced by MAN Technologie AG, Augsburg, Germany, via chemical vapour infiltration of a 2d carbon fibre weave (T800). A prominent case among various applications of this material are screw joints of structural components in re-entry vehicles, e.g. the crew rescue vehicle X38 of the International Space Station ISS. The screws are fixed in a prestressed condition and applied at temperatures up to 1600°C under low oxygen partial pressure. It has been observed that the screw threads act as stress concentrators, a problem which has to be rationalized in order to avoid damage initiation. Thus, quantitative informations about notch sensitivity and deformation processes at stress concentrations are preconditions for an improved dimensioning and layout of the components.

The intrinsic reinforcing properties of the material are evaluated using a sophisticated fracture mechanical test procedure under various loading conditions. The procedure is also applied at ambient conditions as a reference state. Acoustic emission analysis supports the identification of inelastic phenomena at well defined loading conditions. It is indicated that a certain amount of matrix microcracking and interface friction occurs already in the apparently linear elastic state. Numerical exploitation of the complete test procedure reveals the intrinsic reinforcing capability of the material which can be used for the prediction of the materials behavior under more complex loading conditions of real components. Equivalent loading conditions are then applied at elevated temperatures (1200°C – 1600°C) under controlled atmosphere. Deviations in the load-displacement behavior and fractographic analysis indicate specific high temperature damage mechanisms which are discussed in detail. The results are compared to application relevant high temperature testing of CMC screws and first conclusions for life time prediction are drawn.

## **Notch Sensitivity of Woven Ceramic Matrix Composites under Tensile Loading – An Experimental, Analytical and Finite Element Study**

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This paper investigates the stress concentrations associated with circular notches in woven ceramic matrix composites (CMCs) subjected to uniform tensile loading. The CMCs were composed of Nicalon silicon carbide woven fabric in SiNC matrix manufactured through polymer impregnation process (PIP). Several combinations of hole diameter/plate width ratios and ply orientations were considered in this study. In the first part, the stress concentrations were calculated measuring strain distributions surrounding the hole using strain gages at different locations of the specimens during the initial portion of the stress-strain curve before any microdamage developed. The stress concentration was also calculated analytically using Lekhnitskii's solution for orthotropic plates. A finite-width correction factor for anisotropic and orthotropic composite plate were considered. The stress distributions surrounding the circular hole of a CMCs plate were further studied using finite element analysis. Both solid and shell elements were considered. The experimental results were compared with both the analytical and finite element solutions. An extensive optical and scanning electron microscopic examinations were carried out for identifying the fracture behavior and failure mechanisms of both the notched and unnotched specimens. The stress concentration factors (SCF) determined by analytical method over predicted the experimental results. But the numerical solution underpredicted the experimental SCF. Stress concentration factors are shown to increase with enlarged hole size and the effects of ply orientations on stress concentration factors are observed to be negligible. In all the cases, the crack initiated at the notch edge and propagated along the width towards the edge of the specimens.

## Self-healing SiC/SiC composite behaviour under high temperature cyclic fatigue in air

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Groupe d'Etudes de Métallurgie Physique et de Physique des Matériaux  
GEMPPM UMR CNRS 5510, INSA de Lyon, France

Jet engines development programs require more and more high performance levels in materials for spatial and aeronautical applications. In many of these applications, subjecting long-fiber-reinforced ceramic matrix composites (CMCs) to stresses larger than the matrix cracking stress will result in the ingress of the environment to the interior of the composite, particularly in the degradation of both fiber coating (pyrocarbon) and the fibers.

One method to protect it, is to introduce a barrier material in a self-healing matrix and an external sealing coating to reduce the oxygen diffusion into composite. Indeed the ceramic barrier material can be added to the matrix and react with oxygen to produce a sealant glass that inhibits oxidation. This technology has been applied to SiC fibre-reinforced SiC matrix composites (SiC/SiC), fabricated by a CVI process (SNECMA Division Moteurs Fusées, Bordeaux, France). These composites have been tested on cyclic fatigue at high temperature in air, taking into account environmental effects, in order to study damage accumulation resulting from mechanical fatigue and oxidation, and to evaluate the lifetime duration.

The first results showed high residual properties after cyclic fatigue at 1200°C during 100H and so exhibit a good efficacy of the glasses against fibers oxidation.

Reference (without cyclic fatigue) Tensile rupture stress at 25 °C	Residual rupture stress after cyclic fatigue in air during 100 H	
	Tensile/Tensile (0/170 MPa)	Tensile/Compression (170/-50 MPa)
340 MPa	280 MPa	300 MPa

## Mechanical behaviour and failure of enhanced Hi-Nicalon™ reinforced silicon carbide composites in tension creep and fatigue

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**Keywords:** creep, fatigue, high temperature testing, SiC-SiC, Hi-Nicalon, BN interface, fracture behaviour

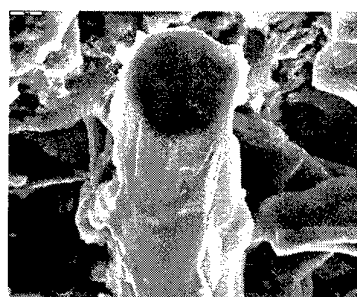
Monotonic tension, tensile creep, high and low cycle fatigue tests of a Hi-Nicalon reinforced SiC matrix CMC were conducted in air at room and elevated temperatures (1000°C, 1200°C and 1400°C). The material (supplied by Lanxide Corp., now Honeywell Advanced Composites Inc., Delaware, USA) has a matrix of chemical vapour infiltrated silicon carbide reinforced with satin woven Hi-Nicalon SiC fibres, which have a BN coating.

The tensile strength of the material decreased from approximately 300MPa at room temperature to ~210MPa at 1400°C. Young's modulus drops to a minimum (125GPa) in the 800 to 1000°C temperature range as compared to the values at the extremes – 150 to 180 GPa. Low cycle fatigue lives increase dramatically when the stress applied drops below the matrix cracking stress, which is just over 100MPa. Examination of the fracture surfaces shows a classic fatigue failure surface, with an area of fatigue damage (short fibre pull out lengths) on one side of the sample, accompanied by an area of longer fibre pull out associated with an over load situation leading to final failure. Closer examination of the fatigue area, reveals wear patterns on the fibres caused by cyclic degradation. Stepped fracture surfaces appear in parts of the weave where fibres are not aligned parallel to the direction of the applied stress.

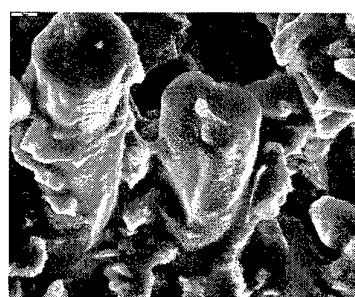
An attempt is made to assess the 'self protection' capacity of the BN interface through analysis of creep data and specimens.



LCF3 – 1200 °C fatigue test.  $f=1$   
Hz,  $R=0.1$ ,  $\sigma_{\max}=200$  MPa



LCF3 – 1200 °C fatigue test.  $f=1$   
Hz,  $R=0.1$ ,  $\sigma_{\max}=200$  MPa



LCF3 – 1200 °C fatigue test.  $f=1$   
Hz,  $R=0.1$ ,  $\sigma_{\max}=200$  MPa

Figure 1; Fracture surface and fibre wear in a LCF specimen tested at 1200°C under a load of 200MPa showing wear damage to fibre surfaces.

## **Creep Behaviour of a 2.5D Woven Composite Material SiC/SiC**

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Keywords: CMC, Creep, SiC/SiC, Interfaces, Nanoindentation.

This paper presents results of creep testing performed with a ceramic matrix composite in which a SiC matrix with boron additions has been reinforced with Hi-Nicalon<sup>TM</sup> SiC fibres.

The fracture surface and longitudinal and transversal sections have been analysed in order to define the deformation, fracture and damage mechanisms, and their relation with the different test conditions (115-300 MPa, 1000-1300°C).

After creep testing the interfacial behaviour has been studied from fibre push-down tests performed with a nanoindentation system. All the tests have been performed on fibres surrounded only by matrix.

For two samples tested at 1000 and 1100°C the interface was initially cohesioned whereas for a sample tested at 1300°C the interface is partially decohesioned. Moreover, interface for sample tested at 1100°C is modified when compared with sample tested at 1000°C because only sudden debond is observed.

Several sudden and gradual debonds are observed. This behaviour occurs in all the tested samples, even for the 70% of the fibres that showed initially a static friction shear stress.

Various fractographic aspects, such as fibre and bundle pullout, crack density, crack pattern, and interfacial mechanical properties are measured in order to define damage maps and the material behaviour at different test conditions.

## CMC creep mechanisms under argon

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**Keywords:** creep mechanism, multiscale and multitechnic analysis, ceramic matrix composites

The aim of this paper is to present from a material science approach the main mechanism which governs creep of ceramic matrix composites made with a "monolithic" ceramic matrix –  $C_rSiC$ ,  $SiC_rSiC$ ,  $SiC_rSiBC$  – in a temperature domain lower than 1673K and a stress domain lower than 250 MPa, when these composites are tested under argon. These materials were reinforced by ex-PAN carbon fibers,  $C_b$  and Nicalon NLM 202 or Hi-Nicalon silicon carbide fibers,  $SiC_f$ .

From the mechanical tests on the one hand, and from multiscale (mesoscopic, microscopic, nanoscopic) observations by SEM and TEM/HREM + EDS analysis, and from morphological analysis by automatic image analysis (AIA) on the other hand, a creep mechanism is proposed for CMCs with 2D architectures in three steps:

- ① development, or creation and development of matrix microcrack networks in transverse yarns, until their saturation,
- ② under stress and temperature there is the opening of the microcracks leading to a partial debonding between longitudinal yarns and matrix of transverse yarns,
- ③ these important inter-yarn cracks will appear along the longitudinal fibers, allowing in the case of CMCs with  $SiC$  fibers the fiber creep (if the applied temperature is higher than 1373K); the opening of these inter-yarn cracks leads to the rupture of the specimens.

That illustrates that we call the damage-creep mechanism which acts when diffusion phenomena and/or dislocation motions are not still in process.

## TRANSIENT CREEP BEHAVIOR IN ENHANCED SiC/SiC COMPOSITES

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The advantages of CMCs are high fracture toughness, high thermal shock resistance, notch insensitivity and no scale effect compared to monolithic ceramics. Furthermore, it is more convenient to manufacture large components with CMCs than monolithic ceramics. The good properties of CMCs are based on the use of weak interfaces e.g., carbon interphase in SiC/SiC. However, the carbon layer leads to low oxidation resistance at high temperatures. To overcome this problem, a glass-forming, boron-based particulates can be added to the matrix that reacts with oxygen to produce a sealant glass that inhibits oxidation of carbon layer. This technology has been applied to SiC/SiC composites. The modified SiC/SiC in this way was called the Enhanced SiC/SiC composite.

Creep tests of Enhanced SiC/SiC composites were carried out in pure argon and air at 1200-1400 °C. The stress-strain hysteresis loops during creep were studied by partial unloading to examine evolution of creep damage. Transient creep behavior appears and dominates creep life. There is no steady state creep stage and little tertiary creep at some stress and temperature conditions. Creep strain rates are correlated with time, stress and temperature to find a creep equation. The stress exponent and activation energy for creep increase with creep time. They are close to the values for fiber's creep at long creep time. A transition in creep mechanism from visco-plastic flow in matrix dominated mode to creep in fiber dominated mode is proposed. Creep resistance of Enhanced SiC/SiC in air are higher than in argon. The creep-environment interaction in the SiC/SiC composites was discussed based on macroscopic properties and microscopic analysis.

## **Microstructure, composition, and strength of ceramic joints between SiC/SiC<sub>f</sub> parts**

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### Ceramic joints, preceramic polymers, silicon carbide, HREM, electron energy loss spectroscopy

SiC-based ceramic composites are promising structural materials in particular for future thermonuclear fusion reactor applications, as they exhibit a low radioactivity by neutron transmutations, a high stability after the reactor shut-down, good high-temperature properties, a low plasma contamination, and a low specific weight. Especially in the case of SiC fiber reinforced SiC composites (SiC/SiC<sub>f</sub>), suitable joining techniques need to be developed in order to be able to fabricate large components or complicated structures exhibiting the required properties. A possible joining technique that has been recently proposed is the use of preceramic polymers (with or without powder fillers).

This paper reports the investigations on the microstructural and nanochemical features of the interlayers in joined SiC/SiC<sub>f</sub> bodies (2D and 3D fiber texture, CVI matrix), as revealed by transmission and analytical electron microscopy down to the atomic level. The ceramic joints were obtained using different preceramic polymers, a silicone resin (SR350, methyl-hydroxyl-siloxane) and a polycarbosilane (HPCS), and heat treating the samples at 1200°C in inert atmosphere. Joints obtained with the addition of  $\beta$ -SiC filler powder (diameter < 1  $\mu$ m) to HPCS, and possessing higher mechanical strength, were also analyzed.

The high-resolving analyses demonstrated that the joining material was a silicon oxycarbide amorphous ceramic in the case of SR350, and a dispersion of nanometre-sized SiC particles in a glassy matrix in the case of filled HPCS. The observations revealed that no chemical reactions occur between the SiC bodies and the inorganic joining material, i.e., the joining effect is caused by adhesive bonding.

The relationship between the features of the interlayers and the mechanical strength of the joints will also be discussed.



## Microstructural investigations of Ceramic Matrix Composites by Raman Microspectroscopy

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Ceramic Matrix Composites (CMCs) are potential candidates for thermostructural applications. Their high temperature properties tightly depend on the nature (i.e., the chemical composition, the structure and the mechanical properties) of the fibers, the matrix and the interphase. Raman microspectroscopy (RMS) is a non-destructive technique, which provides qualitative and quantitative information, at the micrometer scale, on the phase composition (either amorphous or crystalline), the crystalline state, the texture and, in some cases, the stress/strain state of a material.

In the present study, two examples of the application of RMS to the analyses of CMC's constituents are presented.

In the first example, boron nitride coatings prepared by the chemical vapor deposition from a ( $\text{BX}_3$ ,  $\text{NH}_3$ ,  $\text{H}_2$ ) gas mixture have been investigated. The Raman spectral features of the coatings vary with their crystalline state. The frequency and the width at half height of the  $\text{E}_{2g}$  intra-layer mode both increase when the size of the coherent domains ( $L_a$ ) decreases. A correlation between the spectral parameters ( $\nu_{\text{E}_{2g}}$  et  $\Delta\nu_{\text{E}_{2g}}$ ), the CVD-processing conditions ( $\alpha = Q_{\text{NH}_3}/Q_{\text{BX}_3}$ ) and of eventual post-heat treatments has been established.

In the second example, SiC/SiC multilayer composites have been studied. The CVI matrix consists of alternating stoichiometric SiC and two other  $\text{SiB}_x\text{C}_y$  phases of different composition. RMS profiles have been recorded from the cross section of a fiber and its matrix sheath in the composites. The sequence of the various matrix layers has been clearly identified and the microstructure of each layer qualitatively evidenced by RMS.

## **Mechanical Properties of C/C-SiC – Ceramics**

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A woven 2D reinforced composite of carbon fibres processed in a (CVI)-SiC matrix has been investigated by means of different testing methods in order to gain information about the degree of damage in dependence of selected loading and environmental conditions.

The composite was first loaded under tensile stress conditions, and subsequently characterized comprehensively in relation to the damage stage and the fibre properties.

Micro Computed Tomography (MCT) experiments have been performed at the composite after different degrees of load have been applied. MCT is a non destructive technique and delivers a three-dimensional picture of the inherent structure of the composite in the micro- and meso- range. The quantitative analysis of defects in relation to their size and distribution at different stressed samples will be shown.

Light, confocal and electron microscopy of the composite fracture surface and the individual fibre surface of tensile stress rupture samples were used to find out the significant mechanisms responsible for the mechanical failure behaviour of the composite.

Additionally, a D.C. potential drop technique will be described which has been set up to monitor continuously the damage process passing by in the stress-strain experiment. A correlation of the measured conductivity of the samples with different loading levels has been observed which will be discussed in more detail.

Keywords: ceramic composite, mechanical properties, computed tomography, damage characterisation

## Phenomenological Investigations on C/C-SiC Specimens with NDT Methods

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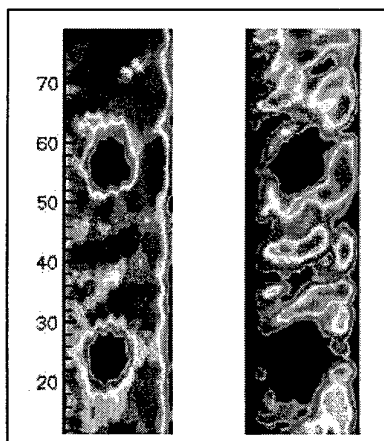
Different kind of continuous fiber reinforced ceramic matrix composites (CMC) are under development for use in advanced structural aerospace and terrestrial applications that require very high temperature materials. Although they offer very high potentials technical shortcomings must still be overcome before CMCs are widely used for example in complex shaped thermostructural applications. Significant barriers to progress are for example: lack of engineering data, knowledge about damage detection/development and not at least understanding of damage mechanism in these kind of materials.

In the present paper some results of an ongoing research programme on damage detection/development in C/C-SiC materials will be presented. The C/C-SiC material investigated here is a continuous fibre reinforced ceramic matrix composite (CMC) manufactured at the DLR after the in-house developed process based on the pyrolysis of high carbonaceous precursors and the liquid silicon infiltration (LSI process).

The detectability of damages with different nondestructive methods towards characterization of the material during manufacturing, and assess the possible influence of damages under mechanical loading with respect to properties of C/C-SiC that are relevant for the safety of structures, are some topics of this phenomenological investigation. The synergetic evaluation of different NDI results together with the correlation to destructive testings allows a quantitative evaluation of damage and material degradation.

Since load introduction is always a critical aspect in fibre reinforced material structures, the pin loaded specimen is used to investigate the damage development confined to a defined region. The detectability and the analysis by means of NDE e.g., US C-scan inspection is described for damages caused by mechanical tensile loading after different loads or number of tensile fatigue cycles at room temperature.

Keywords: NDT, LSI-Process, damage development, damage detection



US C scan pictures of a pin loaded  
Specimen: 0 load cycles (left) and  
3.6e6 load cycles (right)

## Thermal Response and Oxidation Behavior of Si-Ti-C-O (Tyranno<sup>TM</sup>) Fiber / Si-Ti-C-O Matrix Composites under High Enthalpy Convective Environment

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Keywords: Silicon carbide, Arc jet facility, Oxidation, 3-D fabric, Thermal protection system

National Aerospace Laboratory of Japan (NAL), Ube Industries Ltd., Shikibo Ltd., and Kawasaki Heavy Industries Ltd. have conducted a joint program to develop continuous fiber reinforced ceramic matrix composites (CMCs). The composites contain Tyranno<sup>TM</sup> Lox-M fiber (Ube Industries Ltd., Si 54%, Ti 2%, C 32%, O 12%, mass%) with an additional surface modification in order to improve interface properties. The composites exhibit excellent tensile and creep strengths up to 1200°C, and they are referred to as "NUSK-CMCs" from the initials of the collaborators.

We have attempted to apply NUSK-CMCs to thermal protection system of a future reusable space vehicle. For the purpose, thermal response and oxidation behaviors of NUSK-CMCs were evaluated under atmospheric re-entry condition. This test series was conducted by using an arc wind tunnel with a 750 kW plasma generator in NAL. Two kinds of fabric architectures, *i.e.* orthogonal 3-D woven fabric (Z-Plus<sup>TM</sup> SCL) and stitched plain fabric laminate (Z-Plus<sup>TM</sup> Netshape) were prepared.

Cold wall heat fluxes ranged from 0.8 to 1.8 MW/m<sup>2</sup>, and impact pressures at a stagnation point were between 15-27 kPa. Maximum surface temperatures achieved to 1300-1650°C in the test conditions. The measured surface temperatures were far lower than the temperatures predicted by simple numerical calculations. The cold wall heat fluxes reflected a finite catalytic surface because the surface of the calorimeter was made of constantan. Therefore, it should be noticed that the cold wall heat fluxes are not actual value for the composites because of the catalytic effects.

When the surface temperature was lower than 1600 °C, no surface recession was observed after arc jet testing. However, a rapid temperature rise occurred around large pores in the composite without glass sealant under high heat flux condition. In contrast to this, such a phenomenon was not observed in the glass sealed composite. Thus, the glass sealant was effective for the stable aerodynamic heating on the composite surface.

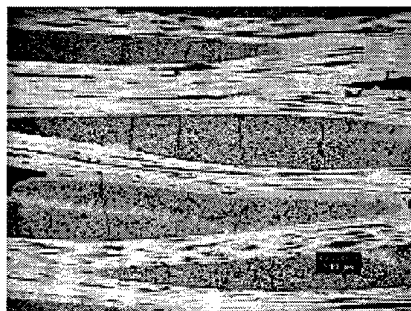
In the experiments, little surface recession was recognized below 1450°C at surface temperature and above 5 kPa in oxygen partial pressure at the stagnation point. Therefore, passive oxidation was dominant under the heating condition. Passive / active oxidation boundary of the composite agreed with the Balat's theory for silicon carbide under the present experimental condition. A small amount of mass loss was observed just above 1500 °C, which was due to decomposition of Si-Ti-C-O fiber and matrix.

## Mechanical Properties of C/SiC Ceramic Matrix Composites (CMCs) for Space Transportation Propulsion Applications

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Keywords: CMCs, C/SiC, mechanical properties, oxidation

The National Aeronautics & Space Administration (NASA) is pursuing the use of ceramic matrix composite (CMC) components in advanced Reusable Launch Vehicle (RLV) propulsion applications. The CMC components are being developed by NASA to enable significant increases in engine performance and safety, and to reduce the cost of transporting payloads to orbit. Safety gains could be realized through the use of durable CMC components having higher specific strength and increased temperature margins. Cost reduction could be achieved by using lightweight, long-life CMC components/systems with higher temperature capability than superalloys to enable higher performance propulsion systems (increased thrust to weight). Carbon fiber reinforced silicon carbide matrix (C/SiC) composites are the primary CMCs of interest for a variety of RLV propulsion applications. These composites have typically been fabricated by depositing an interface coating and a SiC matrix via chemical vapor infiltration (CVI) onto a carbon fiber cloth lay-up. The properties of these C/SiC composites can be modified by changing the fiber, the interface, and/or the ceramic matrix. The identification of a combination of constituents yielding improved durability is critical to the development of improved materials.



Microstructure of a typical CVI C/SiC CMC.

The mechanical properties of several different types of C/SiC materials were determined, in order to assess the suitability of these materials for further development. Stressed oxidation tensile tests were performed as screening tests to assess relative durability of the composites in oxidizing environments. Microstructural characterization of the degraded materials was performed in order to identify the damage mechanisms. The results are reported in this paper.

## CORROSIVE BEHAVIOR OF FIBROUS HOT GAS FILTER IN A MODEL ATMOSPHERE FOR REFUSE INCINERATION

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**Keywords:** fabric filter, hot filter, corrosive behavior

High performance hot gas filters are required in the fields of refuse incineration and thermal electric power plant. The key problems on demand for hot gas filter are resistant to chemical attack of hot dust, which is carried by exhaust gas after burning of industrial waste and coals, as well as resistant to wetting of melted component in the hot dust.

2D satin weave fabrics made from the  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-B}_2\text{O}_3$ (3M-440), and SiC fibers were used as elements of hot gas filter materials. Corrosion tests of the hot gas filter materials against to model dust( $\text{Na}_2\text{SO}_4/\text{NaCl}=1/1$ )and real dust were carried out in a manner that the fabrics, which were covered with the dusts, were heated at 750 and 850°C for 5hs under  $\text{N}_2$ . Corrosion tests of the filter materials against to model exhaust gas [ $\text{O}_2$ (15.9%),  $\text{N}_2$ (75.2%),  $\text{H}_2\text{O}$ (8.8%),  $\text{HCl}$ (0.044%),  $\text{SO}_2$ (0.0044%) by volume] were performed at 850°C for 200h.

In the case of the 2D 3M-440 fiber fabric, several kinds of oxides such as  $\text{Cr}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{SiO}_2$ ,  $\text{Cr}_2\text{O}_3/\text{SiO}_2$ , and  $\text{LaCrO}_3$  were coated on the fabrics, so as to protect for chemical attack of the dusts as well as the model exhaust gas and to resist for wetting of melted component of the hot dust. In the chemical attack test of the dusts at 750°C, 5h,  $\text{Cr}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3/\text{SiO}_2$ , and  $\text{LaCrO}_3$  coated fabrics well withstood for the chemical attack of the dust and resisted to wetting of the dust. However, in the attack test at 850°C, 5h, almost all the oxide coated fabrics except  $\text{Cr}_2\text{O}_3$ , and  $\text{LaCrO}_3$  coated ones were attacked by the dusts. A little attack for the model exhaust gas was observed in all coated fabrics.

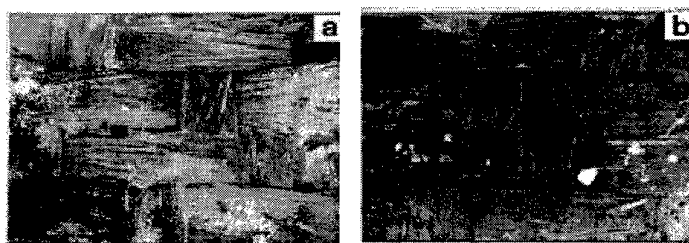


Fig. Optical micrographs of  $\text{LaCrO}_3$  coated 2D-440(3M) filters after heating with real dust under 750°C, 5h(a) and 850°C, 5h(b), respectively.

## **Development of a High-Temperature, High-Pressure Test System for the Tensile Evaluation of Advanced Materials**

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The development and deployment of a new generation of advanced gas turbine engines will depend on the availability of materials capable of withstanding severe conditions of stress, temperature and environment that exist in the combustor, transition sections, gas ducts, vanes and blades. Recently it has been documented that some of the most mature candidate materials for these applications (e.g.- SiC and Si<sub>3</sub>N<sub>4</sub>) experience severe degradation when exposed to actual engine operating conditions. These results have prompted work on the development of environmental barrier coatings and alternative material systems to alleviate this problem.

This poster presentation will describe a test facility that was developed to evaluate the durability of candidate materials for these applications, and for generating data relevant for the formulation of life-prediction algorithms. Results will be presented from the evaluation of ceramic matrix composites at temperatures up to 1200°C and 2 atmospheres of pure steam.

**KEYWORDS:** test facility, high-temperature, high-pressure, steam, mechanical testing

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# **A CONSTITUTIVE MODEL FOR THE DESIGN OF FIBROUS CERAMIC MATRIX COMPOSITE STRUCTURES**

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The development of structural analysis codes aimed at optimizing the design of components made of fiber reinforced ceramic or carbon matrix composites (CMCs) requires a proper description of their non-linear mechanical behavior. These nonlinearities are related to the progressive development of damage phenomena which are highly anisotropic in nature. In the literature, limited effort has been directed at modeling the mechanical behavior of CMCs under multiaxial loading conditions.

The present paper discusses a constitutive model of the mechanical behavior of CMCs submitted to multiaxial loading under plane-stress conditions. This model lies within the framework of Continuum Damage Mechanics for the description of damage accumulation, and the approach to plasticity for the description of residual strains induced by the onset of damage. Damage description relies on the use of a phenomenological internal damage variable defined as the change of the compliance tensor induced by any given loading. Microstructural observations of the damage modes taking place under various mechanical loadings provide qualitative data allowing us to formulate physically founded simplifying hypotheses. The evolution laws of scalar damage variables derived from the components of the compliance tensor are established within a classical thermodynamic framework. The various phenomena observed under compressive loadings are introduced through the definition of an effective compliance tensor. By way of illustration, this general approach is assessed and validated on two different composite materials, a 2D SiC/SiC and a 3D C/C.

**Keywords:** Fibrous CMCs, Non-linear behavior, Continuum Damage Mechanics, Constitutive law, Multiaxial loadings



## **PROBABILISTIC APPROACH TO THE FAILURE OF CERAMIC MATRIX COMPOSITES**

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In various engineering domains including aeronautics, nuclear industry or motor industry, ceramic matrix composites (CMCs) are being investigated extensively in order to provide reliable materials able to work under severe service conditions (high temperature, aggressive environment, ...). CMCs are capable of a highly non-linear stress-strain behavior reflecting the accommodation of deformations and a damage tolerance. Various microstructural mechanisms influence the mechanical response and the lifetime. Damage involves multiple microcracks or cracks that form in the matrix and then are arrested by the fibers. Ultimate failure results from fiber breaks. Formation of matrix cracks and fiber failures are random brittle failure phenomena as a result of the presence of populations of fracture inducing flaws distributed randomly in the matrix and in the fibers.

The present paper investigates first the sensitivity of a 2D woven SiC/SiC composite to flaw related phenomena and to scale and stress-state effects. For this purpose, experimental failure data were generated using tensile and bending tests performed on batches of test specimens having different dimensions and stressed volumes. Then, a failure model based on ergodicity of the critical local stress field was proposed on the basis of the trends evidenced by the experimental results.

Key words : fracture, probabilistic methods, strength, scale effects, non-oxide CMCs

## Morphological quantification of damages in CMCs

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Keywords: automatic image analysis, damage morphological parameters, damage mechanics, ceramic matrix composites

In the case of ceramics and ceramic matrix composites if the applied temperature and stress are not high enough to permit dislocation motions and/or diffusion phenomena, one only observes brittle damages such as microcracks, grain or fiber debonding, fiber or yarn pull-out, crystal or fiber or yarn bridging.... To explain and model the rupture or creep behavior of these materials, the damage mechanics as proposed by Kachanov (1958) and Rabotnov (1969), has to be used. It leads to the damage parameter  $D$ , calculated from the change in "one" of the elastic moduli, when un-loading re-loading loops are performed during the mechanical test.

The use of automatic image analysis methods on the surface ( or in the bulk) of specimens solicited in stress and/or temperature permits to quantify, from a morphological point of view, the damages and their evolution under solicitations.

So one can access, for example, to the surface area of the matrix microcracks and of the yarns, to the opening of these matrix microcracks, ... and to follow the change of these parameters as a function of the experimental parameters (time, stress, temperature, environment). It corresponds to that we call morphological damage parameters, that have now to be introduced in the damage mechanics formalism.

Examples will be given in the case of  $C_f$ -SiC,  $SiC_f$ -SiC and  $SiC_f$ -SiBC composites, creep tested in tension up to 1673K and 220 MPa.

## Physically Based Failure Criterion for Long-Fibre Reinforced Ceramics

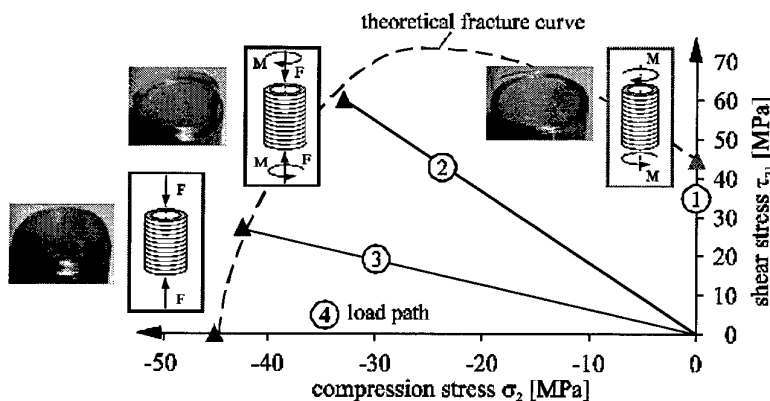
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**Keywords:** reinforced ceramics, fracture behaviour, failure criterion, simulation, combined loads

The extreme lightweight potential of modern long-fibre reinforced ceramics for the application in components under complex thermomechanical loads can only be used optimally, if the anisotropic fibre reinforcement is designed according to the acting loads. For this purpose, on the one hand the temperature dependent anisotropic properties of these materials have to be determined experimentally. On the other hand, the component optimization requires adapted analytical and numerical simulation techniques as well as suitable realistic failure criteria.

At the Institut für Leichtbau und Kunststofftechnik (ILK) the temperature dependent stiffness and strength behaviour under multiaxial loads including combinations of tension, compression, bending and torsion was investigated (temperature range 20 °C up to 1600 °C). These data are needed as so called characteristic parameter functions representing the basic input for stress and strain analysis.

Though the calculation of stress and strain distributions of thermomechanically loaded fibre reinforced components has experienced a tremendous improvement in recent years, the determination of bearable combined fracture loads is still difficult. This is due to the fact that the current generalising fracture criteria do not consider the damage which initially occurs in the heterogeneous micro structure. This demands the formulation of realistic macromechanical failure criteria taking microstructural damage behaviour as well as different modes of fracture into account. The new criterion of HASHIN and PUCK considers not only the difference between fibre fracture and inter fibre fracture, but a fracture angle is introduced which also characterises further fracture types in the plane parallel to the fibres.



Comparison of experimentally determined fracture stresses with the theoretical fracture curve

In this criterion, it is taken into consideration that, in accordance to mechanical material behaviour and phenomenological observations, compressive stresses perpendicular to the fibres tend to prevent the formation of an inter-fibre fracture, while corresponding tensile stresses tend to increase the possibility of inter-fibre fracture. Comparisons of theoretical assumptions and experimentally measured data show a very satisfying agreement for unidirectional carbon-fibre reinforced silicon carbide tube specimen, manufactured by liquid silicon infiltration technique.

## **Predicting failure mechanism of SiC/SiC composites as a function of temperature and oxygen concentration \***

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Keywords: SiC/SiC, composites, environmental effects, crack growth, modeling

The subcritical crack growth mechanism of SiC/SiC<sub>f</sub> composites is a function of temperature, stress, environment, loading mode and time as well as other secondary variables. The crack growth mechanisms include oxidation embrittlement (OEM) in high oxygen containing environments, interphase removal (IRM) in intermediate oxygen containing environments and fiber relaxation (FRM) in low oxygen containing environments. The transition between these mechanism is also a function of temperature, stress and time. Experimental determination of the governing crack growth mechanism for a given set of variables requires an extensive experimental program. Also, it is desirable to develop a failure mechanism map that illustrates the crack growth mechanism regimes as a function of these variables. However, this would require a prohibitively large experimental program. Therefore, the failure mechanisms are being modeled as a function of temperature, oxygen and time to reduce the experimental effort required. The modeling effort guides the experimental verification of the failure map and thus result in a much reduced experimental effort.

It has been possible to predict the transition between the FRM and IRM and between the IRM and OEM. The transition between FRM and IRM is defined as the condition at which the crack velocities from these two mechanisms are equal. The FRM model calculates the crack velocity of SiC/SiC based on the creep relaxation of fibers behind the crack tip and bridging the crack. The IRM model modifies the fiber relaxation in the presence of oxygen by the oxidation of the carbon interface material between the fiber and matrix. This interphase recession results in a time dependent debond length that is a function of temperature and oxygen concentration. A model that predicts the oxygen concentration as a function of depth into the crack and rate equations for the C/O reaction are utilized to predict the recession rate and therefore the additional fiber relaxation rate. The transition between IRM and OEM was predicted by assuming that OEM occurs once the SiO<sub>2</sub> layer thickness around the fiber equals the fiber/matrix interface thickness. This condition is assumed to produce a brittle crack growth process the energy absorbing fiber pull-out process is eliminated. The SiO<sub>2</sub> growth rate is a function of temperature and oxygen concentration. The development of the model predictions of the failure mechanism map, the predictions regarding the time dependence of the various regimes and composite chemistry modifications such as B additions will be discussed.

\* Research supported by the Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. Dept. of Energy

## **A CMCs damage model based on micro and macromechanics for high temperatures and complex loadings.**

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**Keywords:** Model, Damage, Micro-cracking, Closure effects, complex loadings

Predicting the behavior of CMCs under complex thermodynamic loading is a relatively open question. Indeed, these composites have several degradation mechanisms which are hard to interpret; these are associated with cracks which are either orthogonal to the loading direction in matrix blocks or oriented according to fiber bundles. Moreover, mechanical behavior is greatly affected by the opening or closing of microcracks. For damage occurring during traction loading, the compressive behavior keeps its initial mechanical characteristics almost intact.

This work is an extension of the models of macroscopic mechanical behavior developed in LMT-Cachan for previous CMCs, SiC/SiC and SiC/MAS-L. Here, provisions have been made to put information from microscopic observations and from models in the literature into our macroscopic model. Moreover, a new description of damage kinematics allows us to take into account more accurately the effects of closing microcracks; the energetic decomposition introduced dissociates the behavior into traction, compression and a part of shear behavior which is not affected by the open or closed state of the cracks. Evolution laws are associated with the different degradation mechanisms in accordance with previously used procedures. Furthermore, the model allows us to evaluate the amount of damage associated with each composite element (matrix block, bundle, and interphase).

This model was applied to a new generation of CMCs with a self-healing matrix called CERASEP A410 and developed by SNECMA Motors. This material is produced from a multidirectional preform composed of Hi-Nicalon<sup>TM</sup> fibers. The self-healing matrix is deposited by the CVI process. This provides a long life expectancy, in excess of one thousand hours under 140 MPa stress at 1200°C temperature and in an oxidizing atmosphere.

The final objective is to model the oxidation/damage coupling. Here, in this version of the model, we have described the creep/damage coupling for a given state of ageing. The identification uses both traditional macroscopic data and additional microscopic information such as the order of occurrence of the different degradation mechanisms deduced from morphological studies. Finally, the model was implemented and simulations were found to fit the experimental macroscopic mechanical behavior, particularly the effect of closing microcracks. Furthermore, we obtained the evolution of damage in matrix blocks, bundles and interphases for all loading types.

### **Acknowledgements:**

This study was performed as part of the research program entitled "Modeling of behavior and longevity for ceramic matrix composites" conducted by SCNEMA Motors, the DGA and the CNRS.

# **Applications**

**Wednesday, October 3<sup>rd</sup>**  
**Afternoon session**

## **Design, Fabrication and Applications of C/SiC and SiC/SiC Composites**

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**Keywords** : CMC - Manufacturing - Life Time Prediction - Design - Applications

Materials improvement is one of the key factors for achieving performance levels targeted by the rocket motors and jet engines development programs.

Snecma Moteurs is providing an unique experience with over 30 years of Carbon/Carbon and Ceramic Matrix Composites development as well as various engine demonstrations and materials upgrades. Various way of introducing a refractory matrix into the refractory preforms have been explored : these processes and their combinations provide a large variety of Thermostructural Composites (CTS) whose characteristics can be tuned to comply with the aimed application needs and constraints.

For long time uses, CMC performances are affected by fatigue and ageing. Mechanical or thermal fatigue, without oxidation or corrosion, is not detrimental to those composites. They can sustain millions of cycles at high stress levels. Chemical effects are of far greater importance, and may modify strongly strength and elongation to rupture. Life time predictions depend upon an accurate knowledge of environmental conditions, then a good set of representative tests.

Powerful mechanical and thermal code are used for optimised design analysis. At high load or elongation levels, non linear stress strain relationship has to be modelled. Stiffness matrix changes can be determined by simple tests, but tension shear interaction needs more sophisticated experiments. Statistical approaches for safety factors are under development and may be of interest for future methodologies.

This paper provides a status of the technology now base lined for the serial production of SEPCARB<sup>®</sup> and SEPCARBINOX<sup>®</sup> parts for space, aeronautic and industrial applications and the progress achieved with the advanced CERASEP<sup>®</sup> opening up new perspective of service.

## **Melt Infiltrated (MI) SiC/SiC Composites for Gas Turbine Applications**

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**Keywords:** Oxidation, Volatilization, Design, Combustors, Shrouds, Airfoils

Silicon carbide fiber reinforced silicon carbide matrix (SiC/SiC) composites are attractive for high temperature applications because of their high thermal conductivity, excellent thermal shock resistance, creep resistance, and oxidation resistance. Melt infiltration composites are made by a near-net shape process involving the infiltration of liquid silicon into preforms of SiC fibers and SiC and/or carbon matrix; silicon reacts with any carbon to form silicon carbide resulting in a fully dense SiC-Si matrix.

Such composites are particularly attractive for hot section components, such as combustors, shrouds, and airfoils, of gas turbines because the payoff of using such materials is high enough to potentially overcome the initial high costs of these materials. The turbine components are currently made of nickel and cobalt base alloys which are actively cooled to keep their operating temperatures significantly below the temperatures of hot combustion gases. Ceramic composites potentially offer an improvement of a few hundred degrees centigrade compared to the currently used super alloys. Because of their higher operating temperature capability, ceramic composites can be used with little or no cooling, and the air so saved can be used more effectively in the turbine, reducing undesirable emissions such as NO<sub>x</sub> and improving the efficiency and the output of the gas turbine. Implementation of these materials in gas turbines is a long process, involving systematic laboratory studies, rig studies that simulate operating conditions in turbines, small engine tests, followed by tests in large gas turbines at a customer site.

This talk will describe the current status of the development of melt infiltration composites for gas turbine applications and potential risks that need to be alleviated for their successful implementation. The risks include the following: surface recession by volatilization of silica as silicon hydroxide; embrittlement of composites by oxidation of fiber coatings; design constraints by low matrix micro cracking stress/strain and by low inter laminar strengths; attachment problems caused by lower expansion coefficient compared to metallic alloys to which ceramics need to be attached; and high cost of composites. Hi Nicalon fiber reinforced composites are the most developed to date. Stoichiometric fibers, such as HiNicalon-S and Tyranno-SA, are also attractive for applications requiring higher temperature capabilities. A number of rig test and engine tests have been performed at GE to show the feasibility of such composites and would be discussed.

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## Development of 3D-SiC/SiC Component Model for HOPE-X (H-2 Orbiting Plane Experimental)

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**Keywords:** SiC/SiC composite, HOPE-X, High temperature component

Heat resistant composite materials, such as a Carbon/Carbon composite (C/C) and a SiC/SiC composite (SiC/SiC), are the candidates for high temperature components of a reusable launch vehicle because of their good mechanical properties and stability at high temperature. Especially, SiC/SiC has an excellent anti-oxidation property even without any anti-oxidation coating which is required for C/C. Therefore SiC/SiC is considered to be attractive for high temperature components used in air because of their long time durability at elevated temperatures over 873K.

In order to fabricate the components with those materials, the accuracy to their configurations is very important. Although the 2D-composites are usually used for the components, they often change their shapes greatly suffering the thermal stresses which occur during heat treatment. On the other hand, a 3D-composite component is expected to be fabricated with an accurate shape. Because the 3D-textile preforms which reinforce the 3D-composites are effective for stabilization of the shape during fabricating process.

In this study, we show the development result of a 3D-SiC/SiC component trial part for HOPE-X (H-2 Orbiting Plane Experimental) which is being developed by NASDA (National Space Development Agency of Japan). The trial part has been fabricated as a leading edge of a tail-wing of HOPE-X with 3D-SiC/SiC to utilize the advantages mentioned above.



A 3D-SiC/SiC component trial part as a leading edge of a tail wing of HOPE-X

3D-measurements during fabrication process and three-point bending test of the specimens cut from it after fabrication have been carried out. The 3D-measurements have shown excellent stability of the shape during fabrication. The values of the bending strength exceed 300MPa. As the result of this study, it is confirmed that 3D-SiC/SiC has a great potential in the application to high temperature components up to 1673K.

# CMC Light Weight TPS and Hot Structures - Key Technology for RLV

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*Keywords: Reusable Launch Vehicle, Hot Structures, Ceramic Matrix Composites, Thermal Protection System*

## Abstract

Within the European Future Launcher Program (FESTIP) all different candidates of future reusable transportation vehicles (RLV) have been investigated. Even if still under discussion as to which system (single or double stage) will be selected as favored concept, each of the vehicles will have control surfaces and hot structural elements on the windward side of the vehicle, e.g. Leading Edges or Nose Caps with temperature levels far beyond the application of metallic structures.

Test Results on structural components made of "low cost" ceramic matrix composites (CMC) showed that this material can be applied on a wide range of thermal protection systems (TPS) including hot structures and even control surfaces of RLV's. CMC panels and hot structures like leading edges, nose cap or fins require lightweight structures which are resistant to high temperatures and can be reused for a certain number of flights with a minimum effort of servicing.

The example of an CMC control surface shows, that

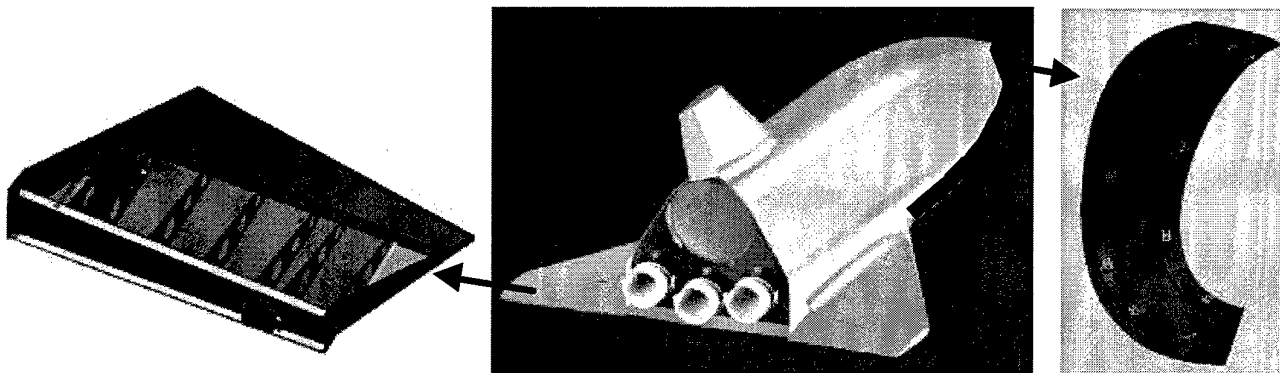
different fields of technologies have to be considered during the development program:

- large C/SiC structures, as recently designed as alternative concept for the elevon of X-33
- load introduction elements and hinge technique
- dynamic seal system between the control surface and the wing/body structure
- the thermal-stress-free fasteners for joining different ceramic components

For all above listed separate technology aspects Astrium has successfully performed verification tests on sub-components level.

Some of the key technology points for a light weight CMC hot structural component have been already successfully applied for the X-38 Nose Skirt panels, even if not already laid out as multi-mission concept.

To wait with the development of one of the structural key-technology until the RLV program has been started may probably lead to the situation that a reusable RLV of the second or third generation (as propagated by NASA) will not be possible since an important part of structural technology is still on the level of expandable launchers.



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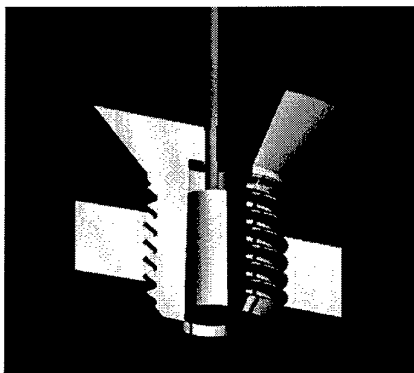
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## Dynamic Qualification of a new CMC Fastener

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**Keywords:** CMC, C/C-SiC, static and dynamic tensile tests, vibration tests, fatigue, high temperature

A lot of engineering effort is currently being invested in the development of Reusable Launch Vehicles (RLV) to lower launch costs and provide economical access to space in such vehicles. CMC's are very favourable materials for hot structures and thermal protection systems (TPS) because of their capability to carry structural loads and to withstand high temperatures up to more than 1600°C. In addition to the improvement of the material itself, the development of suitable joining techniques is very important. Due to high application temperatures, joining methods based on high temperature resistant materials are required. For such purposes a new fastener has been designed at DLR Stuttgart, which combines preferably the functionality of a rivet and a screw



connection whereby all parts of the assembly are manufactured of fibre reinforced ceramic material, strictly speaking of C/C-SiC. In particular the fastener is foreseen to mount outer hot surface structures of re-entry vehicles. At the Institute of Structures and Design of DLR in Stuttgart a test campaign sponsored by ESA took place, which comprised static and dynamic tests under ambient and evacuated high temperature (1550°C) conditions as well as vibration tests. The relation between the low number of expensive specimens and a comparable high number of load cases presents this test campaign rather as a compromise between basic and qualification tests. The aim was to obtain first a preliminary range of life time curves and cautious

assessments of the fatigue limits within two tensile test series under both ambient and high temperature (1550°C) conditions. In a second step shaker tests were performed similar to the random vibration environment of the NASA re-entry vehicle X-38. Summarising the hot tensile tests, the fatigue limits are suspected at a level of about 60 % ÷ 70% of the static strengths. In addition the results of the shaker tests confirm the function of the assembling principle. Further improvements will be achieved by optimisation of several design parameters.

**Brazing of C/SiC and SiC<sub>f</sub>/SiC Composites  
with the BraSiC<sup>®</sup> process for high temperature applications.**

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Key Words : Brazing, composites, C/SiC, SiC/SiC, BraSiC<sup>®</sup> process.

The BraSiC<sup>®</sup> process is becoming the very best standard for brazing SiC based materials for high temperature applications, especially for the realisation of large and complex industrial components. Initially developed for monolithic SiC based materials, the BraSiC<sup>®</sup> process has been recently completed of new fillers, specially adapted for brazing porous C/SiC and SiC<sub>f</sub>/SiC composites. The process allows to control the infiltration of the brazing alloys within the porous composite, that is necessary to assess the filling of the joining by the filler metal. The new BraSiC<sup>®</sup> fillers have been defined to limit as far as possible the thermal expansion mismatch between SiC and the braze. Non-reactive with SiC, the process does not alter the composite, also allowing the reparation of joints, the joints being re-brazed as new after a chemical dissolution of the braze. The brazed joints feature high mechanical strength and good corrosion resistance, comparable to the composite itself : failure generally occur in the composite. Examples of the fabrication of real components will be provided.

## Environmental Properties and Applications of 3D C/SiC and SiC/SiC Composites by Chemical Vapor Infiltration

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Continuous fiber reinforced ceramic matrix composites (CFCCs) are very interest structure materials because of their higher performance compared with super-alloy at elevated temperatures, and higher fracture toughness compared with monolithic ceramics. So far, four kinds of methods developed for fabricating C/SiC and SiC/SiC composite materials are as follows: hot-pressing, reactive melt infiltration, polymer infiltration and pyrolysis (PIP), and chemical vapor infiltration (CVI). In this paper, the authors focused on the three dimensional textile composites and examined the properties at large temperature range of 3D C/SiC and SiC/SiC composite materials produced by CVI, and investigated the applications in various fields.

PAN-based carbon fiber and Hi-Nicalon SiC fiber were employed in the present experiment. Three dimensional (3D) fabric preform was braided by four-step processing. After chemical vapor infiltrated for 30h, the densities of C/SiC and SiC/SiC composites were  $2.1\text{g}\cdot\text{cm}^{-3}$  and  $2.5\text{g}\cdot\text{cm}^{-3}$ , respectively. It was observed that both C/SiC and SiC/SiC composites exhibited the non-catastrophic failure behavior. The stress-displacement curve could be divided into linear stage and non-linear stage before fracture of the composite materials. Microstructure observations revealed that both fiber and fiber bundle could be pulled out during failure composites. Different from the traditional monolithic ceramics, the flexural strength ( $\sigma_f$ ) of the composites was nearly constant when the temperature ranged from room temperature up to  $1600^\circ\text{C}$  because there is no glass phase in grain boundary. In order to determine toughness of the composites, fracture toughness ( $K_{IC}$ ), the work of fracture ( $W$ ) and dynamic fracture toughness ( $\alpha_k$ ) were examined. The results were listed in Table 1.

Table 1. Typical strength of C/SiC and SiC/SiC composite materials

	RT	$\sigma_f$ MPa 1300°C	1600°C	$K_{IC}$ MPa·m <sup>1/2</sup>	$W$ kJ·m <sup>-2</sup>	$\alpha_k$ kJ·m <sup>-2</sup>
C/SiC	460	447	457	20.0	10.0	61.5
SiC/SiC	860	1010		41.5	28.1	36.0

The oxidation experiment of the C/SiC and SiC/SiC composites was investigated in air and combustion environment. The results revealed that the oxidation temperature of  $600\sim 700^\circ\text{C}$  was the most dangerous for the composites, which resulted in the dramatic strength decrease of the composites. However, the flexural strength was nearly not decreased for C/SiC and SiC/SiC composites after 100 times of thermal shock test in the combustion environment.

The abrasive experiment was conducted with oxygen and acetylene flame. The weight loss of C/SiC and SiC/SiC composites was much less than that of some traditional abrasive materials such as  $\text{Si}_3\text{N}_4$ , Mo, BN, C, and C/C. The abrasive rate was  $0.0083\text{mm}/\text{sec}$ .

Combustion chambers have been fabricated with both C/SiC and SiC/SiC composite materials for liquid rocket engines and tested in 150N- propulsion force. Both kinds of composites have successfully tested for the life of 1000 seconds and 3000 pluses in the liquid rocket engine. Aero-engine combustion linings were developed with C/SiC and SiC/SiC composites were successfully tested at the temperature of  $1600^\circ\text{C}$ .

## Progress in SiC/SiC Composites for Engine Applications

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**Keywords:** non-oxide composites, SiC fibers, strength, architecture, creep-rupture, thermal conductivity

The successful application of ceramic matrix composites as hot-section components in advanced gas turbine engines will require the development of CMC material systems that are capable of displaying a variety of key properties related to composite fabrication and thermostructural service. Much initial progress in identifying constituent materials and processes to achieve these properties was made under the former NASA Enabling Propulsion Materials (EPM) Program using near-stoichiometric Sylramic SiC fibers, 0/90 2D-woven architectures, CVI BN interphases, CVI SiC matrix over-coatings, and melt-infiltrated (MI) Si-SiC matrices. The objective of this presentation is to elaborate on recent progress in property optimization for this SiC/SiC system made under the new NASA Ultra Efficient Engine Technology (UEET) Program.

Initial discussion will briefly focus on the key general requirements for CMC hot-section components, such as combustors and turbine vanes. These include the use of composite constituents, geometries, and fabrication processes that yield components not only with the proper thermostructural performance, but also with the proper shapes, sizes, and functional features. Thus fiber types, fiber architectures, interfacial coatings, and matrix constituents and processes must be judiciously selected and tailored for specific components. To facilitate this selection process, NASA UEET has selected a list of key first-order properties that the SiC/SiC composites must display and a list of key tests to evaluate these properties. Emphasis is placed on designing and testing for important constituent-related issues that have been observed or can be envisioned for SiC/SiC components. These include sufficient intrinsic creep and rupture resistance for the fiber and matrix at high temperatures, as well as sufficient oxygen and moisture resistance for the fiber and fiber coating at intermediate temperatures and for the matrix at high temperatures.

Current approaches to achieve improvements in SiC/SiC thermostructural performance are then presented. The validity and magnitude of improvement gained by these approaches are illustrated by composite data taken primarily on tensile specimens removed from as-fabricated SiC/SiC flat panels. The approaches include the development of specific constituent treatments at NASA that significantly improve the creep and environmental resistance of the Sylramic fiber as well as the thermal conductivity and creep resistance of the CVI SiC constituent of the matrix. Also discussed are important observations concerning the beneficial effects of certain variations in the 2D-panel architecture and the detrimental effects of inadvertent carbon in the interfacial region. Thermostructural property models are presented and discussed which support these findings. The CMC data and models are summarized to indicate current UEET directions for further optimization of the SiC/SiC materials and processes for high-temperature CMC engine components.

## **An Improved CMC Family for Long Life Time Functionnning for Jet Aircraft Engine**

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Keywords: self-sealing matrix, CVI, C/SiC, SiC/SiC

A new concept of Ceramic Matrix Composite (CMC), mainly based on the use of a self-sealing technology for matrix and the use of a multilayer woven reinforcement, has been developped by Snecma, for achieving high performance levels targeted by the future jet engines. The main drivers of this development have been to increase both life time and temperature capability of previous C/SiC and SiC/SiC materials using a pure CVI matrix and finishing treatment against oxidation.

First material, which has been developped with this new way, is the CERASEP<sup>®</sup>A410, using the Hi-Nicalon fibers from Nippon Carbon. This has been submitted to a detailed characterization in order to determine thermo-mechanical properties and to evaluate life time duration, using fatigue and creep testing.

Further material development is investigating the use of carbon fiber for economical objectives. The combination of such fibers with the new self-sealing matrix is providing the promising result for long duration applications at high temperature. Such results are permitted by the very high potential of the new matrix.

Specific subelements are being fabricated and tested in order to validate the new technology in term of fabricability and mechanical and thermal behavior.

## **Development of Advanced Combustor Liner Composed of CMC/GMC Hybrid Composite Material**

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Keywords : combustor liner, ceramic matrix composite, glass matrix composite

Research Institute of Advanced Materials Gas-Generator (AMG), which is a joint effort by the Japan Key Technology Center and 14 companies in Japan, has, since 1993, been conducting technological studies on an innovative gas generator that will use 20% less fuel, weigh 50% less, and emit 70% less NO<sub>x</sub> than the conventional gas generator through the use of advanced materials.

Within the AMG project, there has been an R&D program for applying ceramic matrix composite (CMC) liners and glass matrix composite (GMC) to the combustor, which is a major component of the gas generator. Silicon carbide fiber-reinforced silicon carbide ( $\text{SiC}^f/\text{SiC}$ ) is indispensable in the high-temperature parts of the combustor liner because of its high heat resistance, but in the relatively lower temperature region near the connection to metallic parts, the low elastic modulus and high strength of silicon carbide fiber-reinforced glass or glass-ceramic ( $\text{SiC}^f/\text{glass}$ ) makes it more effective and is expected to reduce the thermal stress of actual parts with temperature distribution. Therefore, we conceived a hybrid-structure combustor liner that would combine these advantages. Through our studies we have confirmed the applicability of the selected CMC/GMC hybrid composite as a combustor liner.

In this paper, we describe results of our evaluation of a CMC/GMC hybrid composite material as a combustor liner based on an evaluation of material properties, an analysis of thermal stress, and an evaluation of an actual CMC/GMC hybrid liner with 500 mm in diameter assembled in a combustor and subjected to non-cooled combustion tests in the condition of 1873 K as the liner outlet temperature.



## Heat Exchangers for an Air Turbo-Ram Jet Engine

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The Institute of Space and Astronautical Science in Japan is developing an air-turbo-ram jet engine with an expander cycle (ATREX) for a future reusable space vehicle. This project is targeting a two-stage-to-orbit space (TSTO) plane and the ATREX engine is expected to be used as the first stage engine. This engine is a combined cycle engine performing like a turbojet engine at a subsonic to Mach 2 flight and a fan-boost ramjet in the flight of Mach 2 to 6. Main features of the ATREX engine under development are that the expander cycle is adopted to improve high speed efficiency and high temperature composites, especially C/C composites, are attempted to employ. This engine is estimated to possess sufficient thrust to Mach 6 at a 30 to 35 km altitude provided that high temperature composites can be effectively applied. Since the requirement for ATREX parts is extremely severe due to high temperature environment up to 1500°C, metallic material, such as super alloy, cannot be applied without a cooling system, which inevitably leads to high weight. Now we try to develop the turbine disk and heat exchanger for the ATREX engine. In this paper main idea in the development study of the heat exchanger will be summarized.

According to a preliminary calculation, a heat exchange area of 10 m<sup>2</sup> is required to effectively operate the expander cycle in a 40 mm diameter model. To realize this large heat exchange area, in addition to an conventional insert type exchanger, the walls of the combustion chamber and plug nozzle should be utilized. Heat exchangers usually have complex shape. Thus one of main difficulties in the application of C/C composites to the heat exchanger is how to form such complex shapes. We intend to form heat exchanger by bonding structures. C/C composites can be bonded together by carbon or metal carbide. However the strength of the bonding is extremely low. Hence we must design structures required low bonding strength using three-dimensionally reinforces C/C composites.

The second problem is well known oxidation. The heat exchangers in the ATREX engine is contact with hydrogen on the inner walls of the ducts and steam on the outer walls. Hence the outer surface must be protected by some ceramics coating. We intend to use a Si<sub>3</sub>N<sub>4</sub>/BN multi-layered coating under development, which is effectively prevent cracks in the coating.

The final problem is leakage of hydrogen gas from C/C wall and bonded regions. C/C composites usually include plenty of pores and cracks. The engine system permits total 1 to 3 % of hydrogen gas leakage. To prevent the leakage, it was shown to be effective to apply to impregnate Si into pores and cracks in the C/C composites and thinly plating refractory metal on the surface of the C/C composites.

## **C/SiC Material Evaluation for Aircraft Brake Applications**

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Keywords: aircraft brakes, CVI, PIP, MI

The Ceramic Composite Aircraft Brake (CCAB) Consortium, consisting of the four major competing aircraft brake companies in the USA, Aircraft Braking Systems Corporation, BFGoodrich Aerospace, Honeywell Aircraft Landing Systems, and Parker-Hannifin Corporation Wheel & Brake Division, was created for the purpose of collaborative evaluation of ceramic matrix composites (CMC) for use as a next-generation aircraft brake friction material. CCAB is facilitated by the Ohio Aerospace Institute, and is partially funded by the U.S. Air Force Research Laboratory's Dual Use Science & Technology Office and the Materials & Manufacturing Directorate.

Friction materials for aircraft brakes must satisfy demanding performance and property requirements and must be affordable. The goals of this project are to identify and test SiC-based ceramic composite friction materials that have the potential to provide significant performance improvements relative to current carbon/carbon aircraft brakes. Project goals are a four-fold improvement in wear life, a two-fold improvement in friction coefficient consistency, a two-fold improvement in minimum friction coefficient during rejected takeoff, and a 30% improvement in thermal energy storage capability. Two rounds of sub-scale material fabrication and evaluation will be followed by scale-up of a selected material system for full-scale testing.

In Round 1 of the project, five C/SiC materials fabricated by five different vendors were evaluated. Densification methods were chemical vapor infiltration (CVI), polymer impregnation and pyrolysis (PIP), and melt infiltration (MI). All vendors used the same 3-D carbon fiber preform with a CVI carbon interface coating. Thermal, mechanical, and physical property testing and friction and wear evaluations were completed for each material. Based on the results of Round 1, two PIP materials and one MI material were selected for further evaluation. Results of this testing will be reported in this paper.

## Short Fibre Reinforced CMC Materials for High Performance Brakes

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**Keywords:** CMC Brakes, C/C-SiC, short fibre reinforcement, characterisation, manufacture, design

Bidirectionally reinforced CMC materials are well known by the development of highly complex and thin walled structures for the heat shield of reusable spacecrafts. Since 1988 DLR has developed these so called C/C-SiC materials via a three step manufacturing route. At first a Carbon Fibre Reinforced Plastic (CFRP) green body is manufactured by resin transfer moulding or autoclave technique followed by the pyrolysis of the polymer matrix and the subsequent infiltration of molten silicon in the formed porous Carbon/Carbon preform. For automotive use, especially for high performance brake disks the costs of the fabric materials and the common processing techniques for the CFRP green body are too high for a serial production with high numbers of items. The most promising way to reduce these costs and to simplify the CFRP manufacture is using a short fibre reinforcement and applying hot press technique.

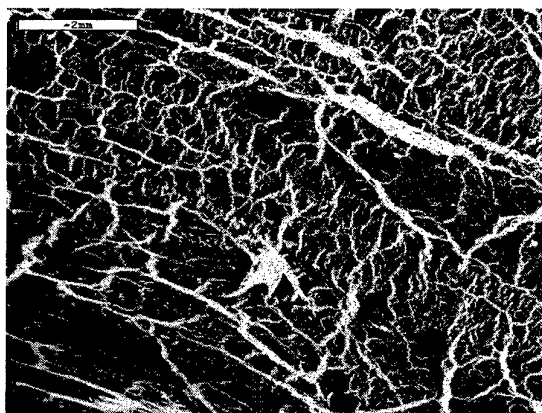


Figure: Microstructure of short fibre reinforced C/C-SiC

In different tribological test campaigns the performance and the excellent wear resistance were proofed. Due to their high thermal stability and their low weight a great leap in brake technology could be achieved, combining non-fading characteristics with better driving dynamics. This paper describes the manufacture of different short fibre reinforced CMC materials as well as patented designs and processing techniques especially for ventilated brake disks. Also, principal materials properties and some specific difficulties in measuring mechanical and thermophysical values will be reported.

## Ceramic Foams and Their Applications

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Keywords: Foams, Ceramic Foams, Carbon Foams, Composite Reinforcement

Open cell forms can be ultra-lightweight and have a variety of applications that is a function of the material composition, porosity, mechanical and thermal properties. Foams which can be insulating or exhibit high thermal conductivity as well as possess good mechanical properties are carbon/graphite, silicon carbide and boron carbide. These foams can be produced in bulk densities ranging from about 0.1 g/cc up to 1.0 g/cc, and depending on the precursor and processing conditions, exhibit good thermal conductivities in the range of approximately 0.2 W/mK to 200 W/mK. The compressive strength is in the range of 2-70 MPa, which is directly proportional to density. These foams have been reinforced in the strut or ligament with graphite fibers and nanotubes which can further increase all properties and particularly compressive strength. The high thermal conductivity foam are excellent for heat transfer applications, while the low thermal conductivity foams provide good thermal insulation. Foams with fiber reinforcements are excellent candidates as a skeleton to produce clutches and brakes. A SiC foam reinforced with carbon fibers infiltrated with silicon or aluminum-silicon alloys are excellent brakes.

## **C/SiC/C Composites for Tribological Application**

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A continuous carbon fibre/silicon carbide – amorphous carbon (C<sub>f</sub>/SiC/C<sub>am</sub>) matrix composite material has been produced by a low-cost manufacturing method. According to this method, the space in a 2-D carbon fibre preform is filled with a SiC powder by a pressure infiltration method. Then the compact body is heat treated at 400°C to form a porous framework, followed by an infiltration step with a liquid phenolic resin. Subsequently the infiltrated resin is carbonised in argon in the temperature of 1000°C. The densification degree, mechanical and thermal properties of the composite material have been measured and related to the microstructure. The brake discs of 144.0 mm in diameter and thickness of 14.0 mm were manufactured from the developed CMC material. The wear-resistance and friction of dry sliding on the disc-on-disc configuration were tested. The developed composites are considered to be a promising material for brake discs for rapid train systems and also can be used as HT-components of chemical reactors, Stirling engines, gas turbines, etc.

### **KEYWORDS**

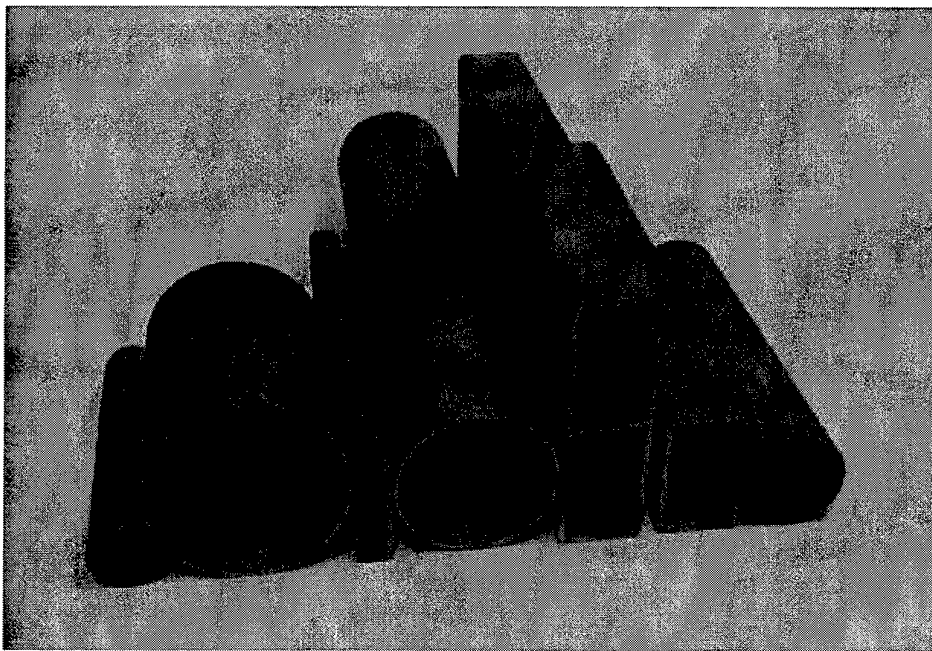
C/SiC/C Composites, Manufacturing Methods, Low-Costs Processing, Carbon Fibres, Silicon Carbide, Phenolic Resin, Pressure infiltration, Resin Infiltration, Pyrolysis Process, Tribological Tests, Automotive Application

## Engineering of CMC Tubular Components

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**Keywords:** CMC tubular components, joining, LSI-processing, properties, heat exchanger

For the development of CMC structural components based on C/C-SiC with different size, shape and geometry the LSI-processing can be used. The processing steps comprise CFRP manufacturing, pyrolysis and final siliconization. Two different processing routes for making CFRPs have been investigated: the compression moulding (CM) as well as the resin transfer moulding (RTM) technique.



CMC tubular specimens with different design manufactured by RTM and CM

In both cases carbon fibre fabrics are wound on a hard core with a variation in fibre orientation angles, especially  $\pm 45^\circ$  and  $0/90^\circ$ . The key factor for the production of delamination-free tubes is the control of pressure and temperature during curing of the resin and during pyrolysis. CM as well as RTM enable the manufacturing of variable wall-thickness, length, radius and fibre angle of tubular specimens in near net shape design. Via in-situ joining of components in the carbonized stage (C/C) it is possible to create reaction bonded samples with good mechanical properties. The choice of the structural parameters like the resin type and fibres as well as the stacking sequence influence the microstructure and therefore the mechanical and thermophysical properties of the tubes which will be reported in this article. CMC tubular components can be used in the environment of high-temperature ( $> 1000^\circ\text{C}$ ) combined with corrosive gas atmosphere e.g. for a new generation of heat exchangers.

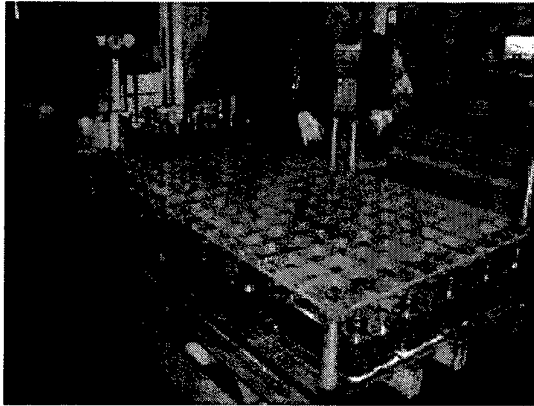
## Applications of CMC-racks for high temperature processes

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Keywords: heat treatment, brazing, sintering, CFRC, contact-reactions, thermal shock

Ceramic Matrix Composites (CMC) like CFRC (carbon fiber reinforced carbon) or CSiC show great material advantages based on the following main material properties: low density, excellent stiffness and strength at high temperatures up to 2800°C according to inert gases or vacuum, low reactivity, extreme low thermal expansion (C.T.E.-value) in fibre direction.

For success in industrial applications like the following three more aspects have to be developed further on: material-commercialisation, design rules and a successful market entry of first



application (mainly in partly conservative industries like aerospace, transportation, mechanical engineering, tool or metal processing industry).

The main target of the Fraunhofer TEG as the engineering specialist and co-operation promoter of the Fraunhofer association is to bring innovative products and processes into the market.

Composite constructions developed since five years ago are now ready for publication and implementation in industrial processes: rack-systems are made

of high temperature materials like metals, oxide ceramics, ceramic coatings and mainly CMCs.

CFRC-rack for brazing (dim. 2000x1000x1000 mm, max. weight 3000 kg; TEG for Modine Europe)

Application fields of the patented CFRC-racks are:

- Heat treatment processes of gear systems, engine

parts; suitable for oil quenching

- brazing processes for e.g. heat exchangers, aerospace parts (see figure above)
- Sintering of ceramics, metals etc.

Common atmospheres are gases like H<sub>2</sub>, N<sub>2</sub>, Ar, He, CO or vacuum processes less 1 mbar. About ten references in different application fields show the advantages and also some problems.

To sum up the main advantages of the new CFRC-racks are as follows:

- Small rack-volumes because of excellent high temperature strength => increased capacity
- Low thermal expansion and high stiffness => excellent position of treated parts
- Lightweight constructions => ergonomic handling and low energy consumption
- Long life cycle => high economic benefit

Some future development based on industrial experience:

- Reducing the porosity of CMCs for processes in contact with fluids
- Establishing ceramic coatings and layers avoiding corrosion and diffusion
- Improving replaceable and economical composite constructions

## CMC Materials for Lightweight and Low CTE Applications

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**Keywords:** Low CTE applications, C/C-SiC, LSI-process, calibration plate, telescope

Carbon fibre reinforced CMC materials, originally developed by DLR for the heat shield of reusable spacecrafts, offer a great applicability for extreme lightweight and thin walled structures combining an excellent strength to density ratio with a close to zero thermal expansion behaviour even at high temperatures. These so called C/C-SiC materials are manufactured via the one shot manufacturing Liquid Silicon Infiltration Process (LSI) by the infiltration of molten silicon into a porous carbon/carbon preform. As no fibre coatings and no re-infiltration steps are necessary, the manufacture is relatively cheap compared to chemical vapour infiltrated CMC materials. Other great advantages of these C/C-SiC materials are their high resistance against corrosion and the possibility of tailoring their thermomechanical properties in a wide range.

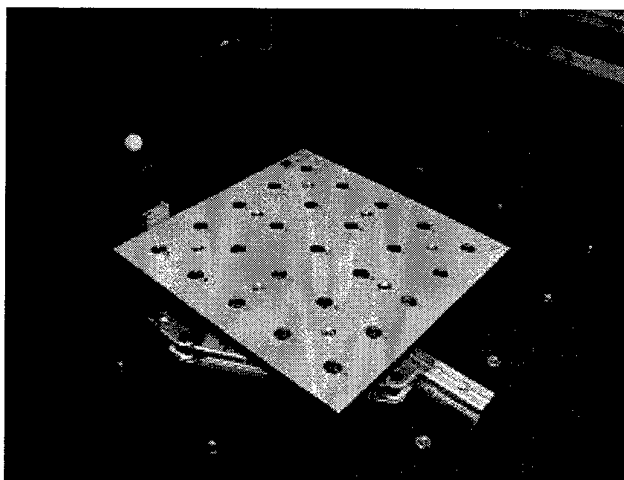


Figure: Calibration plate made of C/C-SiC  
(420 x 420 x 8 mm)

In this paper principal correlations between the thermal expansion and different C/C-SiC materials achieved by varying the raw materials and processing parameters as well as the mechanical and microstructural characterisation of these different material qualities are discussed. Two special applications which require very low and constant CTE values over the temperature will be described exemplarily. C/C-SiC prototypes have been designed, manufactured and tested successfully in collaboration with industrial partners. One is a telescope structure for the data link between satellites based on an optical concept. The other application is a new calibration plate for coordinate measuring machines used commonly in industrial fabrication.



## Cost Analysis for the Manufacture of C/C-SiC Structural Parts

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**Keywords:** LSI-process, C/C-SiC components, cost analysis, manufacture

A novel technology to produce efficiently ceramic matrix composite (CMC) structures has been developed at the DLR. By liquid silicon infiltration (LSI) into carbon/carbon materials, so called C/C-SiC composites can be manufactured. These materials show extraordinary physical properties: heat resistance, thermal shock resistance, good frictional behaviour and excellent mechanical strength.

Low manufacturing costs are a fundamental requirement for a wide industrial usage of CMC materials. The LSI process offers the potential of a cost-effective manufacture of CMC due to low raw material costs and short manufacturing times. Comparatively short processing times result from avoiding any reinfiltration steps and by taking advantage of the high capillarity of molten silicon into porous carbon and the therefore fast reaction time.

Component	Standard plate	Nose Cap	Jet Vanes	Brake Disks
Application Field	Research	Aerospace	Aeronautics	Transportation
Number of Pieces	1-3	< 10	< 1000	> 10000
Construction	Flat Plate	Integral Construction	Single Part	Differential Construction
Dimension	300x300x3 mm <sup>3</sup>	Ø 750 mm	100x60x20 mm <sup>3</sup>	Ø 320 mm

Fig: Overview of the investigated C/C-SiC components

This paper analyses the manufacture costs for exemplary C/C-SiC components produced by DLR's LSI-process. Different application fields have been considered (research, aerospace, aeronautics, transportation). Four components have been chosen, which can be distinguished in terms of design complexity, dimensions and potential manufacturing volume. The most important cost drivers and their influence on the material's price have been determined.

## **Development of Non-contact Damage Detection Method by Electromagnetic Wave**

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**Keywords** : damage detection, dielectric properties, EM-wave

Non-destructive damage detection and evaluation method are an important subject of research for damage tolerance materials such as continuous fiber-reinforced ceramic matrix composite. Recently, a new method for damage evaluation of SiC fiber-SiC matrix composite (hereafter denoted as SiC/SiC) was developed using a damage parameter from tensile stress-strain curve. Non-contact damage detection was conducted by using electromagnetic wave during tensile test, based on the change of dielectric properties of the composite. The damage evaluation method successfully combined the damage parameter with the dielectric properties [1]. However, more detailed studies on this method are needed to improve the accuracy and make quantitative evaluation.

In this study, several types of monolithic  $\text{Al}_2\text{O}_3$  ceramics were used to correlate dielectric properties with volume fraction and distribution of pores. Then, unidirectional SiC fiber reinforced BaO-MgO- $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  glass ceramic matrix composite was used to identify the effect of fibers and interfaces on dielectric properties. Finally, the dielectric properties were used to evaluate damage of 2D SiC/SiC commercial composite. The physical meaning and resolution of the dielectric properties was examined and discussed.

[1] T. Mamiya, S. Zhu, and Y. Kagawa, "Application of Dielectric Properties to Non-Contact Damage Detection for Continuous Fiber-Ceramic Matrix Composites," *Ceram. Eng. Sci. Proc.*, (2001) submitted.

## **A New Data Management System for Ceramic Matrix Composites**

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### **Keywords:**

CFCC - Data Management - Database - CMC

### **Abstract:**

Continuous Fibre Ceramic Composites (CFCC) are tailored for use in high temperature structural applications. With the most recent improvements in processing technologies and despite some limitations with respect to oxidation and/or creep resistance, these materials are now close to industrial applications. To underpin their application potential, CFCC require dedicated, adequate and efficient material data management tools, which allow fast data access for the use in design and analysis. These tools must be adapted to match the CFCC properties and have to account for high elastic anisotropy, damage tolerance and fibre matrix bond strength. The related database has to meet the needs of engineering activities and collaborative research projects where mechanical testing activities are carried out among several partners.

The Ceramic-Matrix-Composite database (CMC-DB) developed at the Institute for Advanced Materials of the European Commission has been designed to fulfil the aforementioned requirements. The CMC-DB system can store experimental data from mechanical tests performed according to accepted standards. The relational database is included in PC stand-alone and client/server versions with intelligent user-guidance running under MS Windows. The first version of the CMC-DB is now available. The database system allows data entry and data retrieval for tensile, creep and low cycle fatigue test data and related mandatory source, specimen and material information. The output options are tables, charts and reports.

Because many experiments carried out with these materials are still falling into the research stage, the CMC-DB can also cope with measurements and data that are not inferred from existing standards *stricto-sensu*. For instance, multi-axial strain measurements (to be used for the determination of anisotropic elastic constants), stiffness evolution for tensile or creep cyclic tests and test data for constituents (single fibre or fibre bundle) can also be entered.

## **A new chart method of assessing the mechanical/thermomechanical behavior of ceramic matrix composites**

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Keywords : CMCs, chart method, micro and minicomposite, multiscale approach

The thermomechanical properties of Ceramic Matrix Composites are classically assessed using two main procedures : The first one starts from macromechanical tests (tensile, compression, flexure) and uses some models which show advantages and drawbacks. The second starts from micromechanical tests (micro and nanoindentation) and the corresponding models. In this case, advantages and drawbacks can also be noticed. In this work, we propose a micro-meso-macro (multiscale) approach to assess the thermomechanical behavior of CMCs whatever the architecture of the fibers. This chart method can be the premise upstream the proposal of a worldwide approach of assessing and comparing the properties of CMCs whatever the supplier and the processing route.

## **Tyrannohex : High Potential Composites for Structural Applications**

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Keywords : CMCs, TyrannoHex, cyclic fatigue,

Tyrannohex composites are newly developed composites and their thermomechanical properties show promising results. These materials are self-bonded oxidized fibers, where no matrix is deposited; the matrix being self-generated by the fibers. A set of mechanical/thermomechanical, cyclic fatigue and creep tests were performed on Tyrannohex. Recently, a new generation of Tyrannohex materials was produced and it shows exceptional behavior. This work will be a retrospective of all the work performed on Tyrannohex with a deep comparison with existing composite systems.